Measurements of Vapor Pressure, Heat Capacity, and Density along the Saturation Line for ϵ-Caprolactam, Pyrazine, 1,2-Propanediol, Triethylene Glycol, Phenyl Acetylene, and Diphenyl Acetylene

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This paper reports measurements made for DIPPR Research Project 821 in the 1996 Project Year. Vapor pressures were measured to a pressure limit of 270 kPa (unless decomposition occurred) for all six compounds using a twin ebulliometric apparatus. Additionally, for ϵ-caprolactam, measurements at low pressures (0.043 kPa to 3.08 kPa) were performed using an inclined-piston apparatus. Liquid-phase densities along the saturation line were measured for each compound over a range of temperatures (ambient to a maximum of 548 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. A critical temperature and the corresponding critical density were determined experimentally for pyrazine. 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), enthalpies of fusion if solid at ambient temperature, 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 $[(1 - T_r)^{n/3}]$. For ϵ-caprolactam, the results of the present measurements were combined with literature values to derive a “Third Law” estimate of sublimation pressures in the region of ambient temperature. All measured and derived values were compared with those obtained in a search of the literature.

Introduction

The papers (Steele et al.[1−3]) 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. (The Project continues today with the ongoing research being carried out within the Physical Properties Research Facility (PPRF) at Oak Ridge National Laboratory.) The objectives of this 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;[4] 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 six compounds studied in the 1996 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[1−3] 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 1−3 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 except the ϵ-caprolactam that was a 99.998 mol % pure sample donated to the project by Allied Signal. Gas−liquid chromatographic (GLC) analyses on the purchased samples gave an average purity of 98 mol %, in agreement with Aldrich specifications. The purchased compounds, except diphenyl acetylene, were purified by

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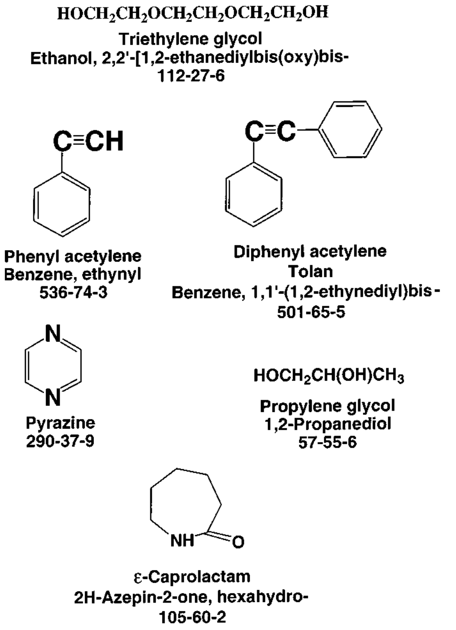

Figure 1. Structural formulas, common names, Chemical Abstracts Service names (provided by the authors), and Chemical Abstracts Service Registry Numbers (provided by the authors) for the compounds studied in this research.

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 except for diphenyl acetylene. 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. Diphenyl acetylene was zone refined (150 passes) and assayed as 98.5 mol % pure by GLC analysis with the main impurity being *trans*-stilbene. Repeated recrystallization from methanol followed by solvent removal just below the melting point resulted in a sample of 99.8 mol % purity that was used in the measurements reported in this research.

All transfers of the purified samples were done under nitrogen or helium or by vacuum distillation. The water 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[5] and the gas constant, R = 8.314 51 J·K^{-1}·mol^{-1}, adopted by CODATA.[6] The platinum resistance thermometers used in these measurements were calibrated by comparison with standard platinum resistance thermometers whose constants were determined at the National Institute of Standards and Technology (NIST). All temperatures are reported in terms of ITS-90.[7,8] 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 ϵ-caprolactam, pyrazine, 1,2-propanediol, triethylene glycol, phenyl acetylene, and diphenyl acetylene are listed in Table 1. The vapor pressures, the condensation temperatures, and the difference 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 ϵ-caprolactam above 550 K, for triethylene glycol above 560 K, for phenyl acetylene above 400 K, and for diphenyl acetylene above 520 K.

Inclined-piston vapor-pressure measurements for ϵ-caprolactam are also listed in Table 1. The inclined-piston values extend the range of measured values down to 350 K, close to the melting point (342.3 K).

Differential Scanning Calorimetry. Two-phase heat capacities $C_{x,m}^{II}$ were determined by DSC for each of the compounds.[9] Heat capacities were determined at 20 K intervals with a heating rate of 0.083 K·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, except pyrazine, extensive sample decomposition precluded attainment of heat-capacity measurements above the highest listed temperatures. For those compounds, only in the case of 1,2-propanediol was the range of temperature sufficient to distinguish between $C_{x,m}^{II}$ and $C_{sat,m}$, and for that compound the results obtained for each cell filling are listed in Table 2. For each of ϵ-caprolactam, triethylene glycol, phenyl acetylene, and diphenyl acetylene, 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.)

Table 2 also contains the results of measurements of $C_{x,m}^{II}$ on pyrazine using three different cell fillings. Measurements showed the presence of a phase transition at ~300 K (see below and Table 2). For pyrazine, measurements in the critical region were possible. An abrupt decrease in the heat capacity associated with the conversion from two phases to one phase was observed during measurements with each cell filling. Since sample decomposition is greatly reduced by employing a single continuous heat source at a heating rate of 0.333 K·s^{-1}, measurements were performed for two further cell fillings using the rapid heating technique. Temperatures at which conversion to the single phase occurred were measured. Table 3 reports those temperatures and the corresponding densities obtained from the mass of sample and the cell volume, V_x, calculated with the equation

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

where $y = (T - 298.15)$ K, $a = 3.216 \times 10^{-5}$ K^{-1}, and $b = 5.4 \times 10^{-8}$ K^{-2}.

A critical temperature and critical density were derived graphically for pyrazine, as seen in Figure 2. Results of measurements on benzene and toluene performed as “proof-of-concept measurements” for these procedures have been reported.[10] The rapid heating method was used previously for critical temperature and critical density determinations

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
					ϵ-Caprolactam						
ip	349.982	0.0430	0.0002	0.0002		d	469.795	13.331	0.000	0.001	0.005
ip	359.979	0.0838	0.0006	0.0002		d	476.706	16.664	0.001	0.002	0.005
ip	369.976	0.1553	0.0004	0.0002		d	482.474	19.952	0.002	0.002	0.004
ip	379.976	0.2776	0.0007	0.0002		d	489.993	25.024	0.000	0.002	0.003
ip	389.972	0.4772	0.0005	0.0003		w	489.980[b]	25.015	0.000	0.003	0.007
ip	399.974	0.7944	0.0002	0.0003		w	497.577	31.174	−0.003	0.003	0.007
ip	409.969	1.2814	−0.0006	0.0004		w	505.211	38.566	−0.006	0.004	0.008
d	419.849	2.0007	0.0000	0.0003	0.033	w	512.892	47.395	−0.007	0.005	0.013
ip	419.968	2.0113	−0.0004	0.0005		w	520.582	57.821	−0.001	0.005	0.023
ip	424.960	2.4933	−0.0008	0.0006		w	528.318	70.115	0.012	0.006	0.037
ip	429.966	3.0738	−0.0008	0.0007		w	536.091	84.504	0.028	0.007	0.052
d	436.468	3.9986	0.0000	0.0005	0.021	w	543.962	101.326	−0.022	0.009	0.038
d	443.910	5.3375	−0.0004	0.0006	0.013	w	551.827	120.77	−0.02	0.01	0.053
d	454.892	7.9988	−0.0002	0.0009	0.009	w	559.720[c]	143.19	0.01	0.01	0.084
d	463.135	10.6651	0.0001	0.0011	0.007	w	567.668[c]	168.98	0.06	0.01	0.119
					Pyrazine						
w	353.704	31.183	0.000	0.004	0.002	w	395.475	120.77	0.00	0.01	0.001
w	359.555	38.559	0.000	0.004	0.001	w	401.584	143.20	0.00	0.01	0.002
w	365.458	47.380	−0.001	0.005	0.001	w	407.739	168.98	0.00	0.01	0.002
w	371.385	57.815	0.000	0.006	0.001	w	413.934	198.47	0.00	0.02	0.002
w	377.360	70.133	0.001	0.007	0.001	w	420.148	231.93	0.00	0.02	0.003
w	383.354	84.520	0.001	0.008	0.001	w	426.411	269.93	0.00	0.02	0.004
w	389.398	101.314	−0.003	0.009	0.001						
					1,2-Propanediol						
d	365.335	2.0036	−0.0001	0.0003	0.038	w	425.488	31.197	0.004	0.004	0.002
d	378.389	4.0020	0.0002	0.0005	0.016	w	431.261	38.565	0.001	0.004	0.001
d	384.179	5.3362	0.0000	0.0007	0.013	w	454.550	84.510	−0.006	0.008	−0.001
d	392.709	7.9944	0.0001	0.0010	0.007	w	460.412	101.297	−0.004	0.010	−0.001
d	399.097	10.6642	−0.0005	0.0013	0.005	w	466.287	120.75	0.01	0.01	0.000
d	404.230	13.330	0.000	0.002	0.004	w	472.187	143.19	0.00	0.01	0.000
d	409.522	16.650	0.000	0.002	0.003	w	478.110	168.99	0.00	0.01	0.000
d	413.927	19.925	0.000	0.002	0.003	w	484.047	198.45	0.00	0.02	0.000
d	419.693	25.017	0.000	0.003	0.002	w	489.997	231.95	0.00	0.02	0.001
w	419.679[b]	25.010	0.006	0.003	0.003	w	495.971	269.95	0.00	0.02	0.001
					Triethylene Glycol						
d	442.026	2.0048	−0.0001	0.0003	0.103	w	510.250[b]	25.032	0.001	0.003	0.025
d	458.274	3.9950	0.0004	0.0005	0.062	w	517.539	31.185	−0.001	0.003	0.028
d	465.589	5.3410	0.0003	0.0006	0.051	w	524.854	38.577	−0.003	0.004	0.030
d	476.326	8.0116	−0.0006	0.0009	0.032	w	532.165	47.368	0.000	0.005	0.033
d	484.300	10.6680	−0.0005	0.0011	0.030	w	539.523	57.822	0.002	0.006	0.036
d	490.778	13.343	−0.001	0.001	0.024	w	546.884	70.101	−0.006	0.006	0.047
d	497.453	16.675	0.000	0.002	0.027	w	554.268	84.512	0.004	0.008	0.055
d	502.965	19.929	0.001	0.002	0.023	w	561.657[c]	101.312	0.054	0.009	0.082
d	510.258	25.040	0.003	0.002	0.023						
					Phenyl Acetylene						
d	312.542	1.9995	0.0003	0.0003	0.053	d	370.780	25.037	0.001	0.002	0.019
d	326.246	3.9918	−0.0013	0.0005	0.029	w	377.116	31.174	−0.004	0.003	0.026
d	332.404	5.3310	−0.0003	0.0007	0.025	w	383.531	38.583	−0.005	0.004	0.033
d	341.532	8.0002	0.0014	0.0010	0.020	w	389.964	47.380	−0.005	0.005	0.044
d	348.369	10.6611	−0.0004	0.0012	0.017	w	396.442	57.800	0.000	0.006	0.060
d	353.909	13.327	0.000	0.002	0.015	w	402.990	70.114	0.008	0.007	0.093
d	359.691	16.676	0.001	0.002	0.016	w	409.567[c]	84.496	0.027	0.008	0.163
d	364.474	19.944	0.002	0.002	0.016	w	416.200[c]	101.282	0.075	0.009	0.281
					Diphenyl Acetylene						
d	439.627	1.9972	−0.0001	0.0003	0.100	d	494.801	13.329	0.001	0.001	0.027
d	457.925	3.9935	0.0010	0.0005	0.057	d	502.478	16.666	−0.002	0.002	0.025
d	466.187	5.3383	−0.0014	0.0006	0.036	d	508.807	19.918	0.002	0.002	0.036
d	478.306	7.9977	−0.0001	0.0008	0.028	d	517.206	25.018	−0.001	0.002	0.042
d	487.418	10.6616	0.0007	0.0011	0.023						

[a] ip denotes inclined piston. 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 observed value of 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 2 and the parameters listed in Table 5, from the observed value of pressure ($\Delta p = p - p_{\mathrm{Wagner}}$). σ is the propagated error calculated using $\sigma(p) = (1.5 \times 10^{-4})p + 0.2$ Pa (inclined piston) or $\sigma(p) = (0.001)\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\}^{1/2}$ (ebulliometer), 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.

for 2-aminobiphenyl,[11] dibenzothiophene,[12] and carbazole and benzofuran.[9]

ϵ-Caprolactam, pyrazine, and diphenyl acetylene are solids at 298.15 K. By judicious choice of starting temper-

Table 2. Experimental Two-Phase Heat Capacities, Derived Saturation Heat-Capacity Equations, and Phase-Transition Enthalpies Derived from DSC Measurements ($R = 8.314\ 51\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

ϵ-Caprolactam (crystalline)
$C_{\mathrm{sat,m}}/R = 0.084T - 6.4$ (in temperature range 290 K to 342.3 K)

ϵ-Caprolactam (liquid)
$C_{\mathrm{sat,m}}/R = 0.051T + 11.4$ (in temperature range 342.3 K to 500 K)
$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(\epsilon\text{-caprolactam}, 342.3\ \mathrm{K}) = 16.2 \pm 0.3\ \mathrm{kJ \cdot mol^{-1}}$

Triethylene Glycol (liquid)
$C_{\mathrm{sat,m}}/R = 0.048T + 25.9$ (in temperature range 303 K to 553 K)

Phenyl Acetylene (liquid)
$C_{\mathrm{sat,m}}/R = 0.040T + 9.8$ (in temperature range 303 K to 393 K)

Diphenyl Acetylene (crystalline)
$C_{\mathrm{sat,m}}/R = 0.085T + 1.7$ (in temperature range 303 K to 335 K)

Diphenyl Acetylene (liquid)
$C_{\mathrm{sat,m}}/R = 0.07T + 12.0$ (in temperature range 335 K to 500 K)
$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(\text{diphenyl acetylene}, 335\ \mathrm{K}) = 21.5 \pm 0.5\ \mathrm{kJ \cdot mol^{-1}}$

	$C_{\mathrm{X,m}}^{\mathrm{II}}/R$		
T/K	m/g = 0.008 861 $V_{\mathrm{c}}{}^{a}/\mathrm{cm}^3 = 0.0522$	m/g = 0.015 273 $V_{\mathrm{c}}{}^{a}/\mathrm{cm}^3 = 0.0522$	m/g = 0.020 513 $V_{\mathrm{c}}{}^{a}/\mathrm{cm}^3 = 0.0522$
		1,2-Propanediol	
313.15	23.5	23.5	23.6
333.15	24.6	24.7	24.7
353.15	25.6	25.5	25.8
373.15	26.6	26.7	26.8
393.15	27.7	27.7	27.7
413.15	28.4	28.6	28.5
433.15	29.8	29.4	29.3
453.15	30.8	30.3	30.1
473.15	32.2	31.3	30.8
493.15	33.5	32.1	31.6
513.15	34.8	33.2	32.3
533.15	36.2	34.5	33.1
553.15	38.0	35.3	33.8
573.15	39.5	36.3	34.6

	$C_{\mathrm{X,m}}^{\mathrm{II}}/R$		
T/K	m/g = 0.011 628 $V_{\mathrm{c}}{}^{a} = 0.0522$	m/g = 0.014 170 $V_{\mathrm{c}}{}^{a} = 0.0522$	m/g = 0.019 796 $V_{\mathrm{c}}{}^{a} = 0.0522$
		Pyrazine Crystals (cII)	
278.15	11.5	11.4	11.5
283.15	11.7	11.7	11.7
288.15	11.9	11.9	11.8
293.15	12.0	12.1	12.1
		Crystals (cI)	
303.15	13.1	13.1	13.1
308.15	13.3	13.3	13.3
313.15	13.5	13.5	13.6
		Liquid	
348.15	17.4	17.2	17.1
368.15	18.1	17.8	17.7
388.15	18.8	18.5	18.4
408.15	19.8	19.3	19.1
428.15	21.0	20.3	19.8
448.15	22.2	21.3	20.7
468.15	23.3	22.4	21.5
488.15	24.5	23.2	22.3
508.15	25.5	24.3	23.2
528.15	26.6	25.5	24.2
548.15	28.0	26.1	25.0
568.15	29.2	27.3	25.6
588.15	31.4	28.9	27.8
608.15	34.7	36.4	32.8
628.15[b]	16.5	23.8	26.0

crystalline (cII) $C_{\mathrm{sat,m}}/R = 0.042T - 0.2$[c]
$\Delta_{\mathrm{cII}}^{\mathrm{cI}}H_{\mathrm{m}}^{\circ}(300.5\ \mathrm{K}) = (0.9 \pm 0.1)\ \mathrm{kJ \cdot mol^{-1}}$
crystalline (cI) $C_{\mathrm{sat,m}}/R = 0.048T - 1.5$[d]
$\Delta_{\mathrm{cI}}^{\mathrm{l}}H_{\mathrm{m}}^{\circ}(325.5\ \mathrm{K}) = (14.7 \pm 0.3)\ \mathrm{kJ \cdot mol^{-1}}$

[a] Volume of cell in cubic centimeters is given for 298.15 K. [b] Values not used in fitting procedures because they are above either the critical or decomposition temperature. [c] In temperature range 268 to 300.5 K. [d] In temperature range 300.5 to 325.5 K.

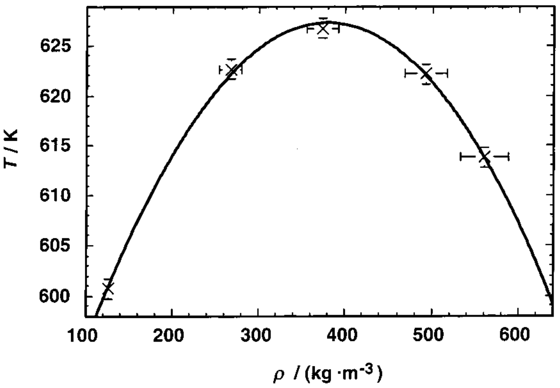

Figure 2. Vapor−liquid coexistence in the region of the critical point for pyrazine. The curve is drawn as an aid to the eye and does not represent any theoretically valid equation. The crosses span the range of uncertainty.

Table 3. Densities and Temperatures Used To Define the Two-Phase Dome near T_{c} for Pyrazine

$\rho/\mathrm{kg \cdot m^{-3}}$	T/K
126.4	600.8
267.2	622.6
373.2	626.8
492.4	622.2
560.0	613.8

ature, the melting endotherms during the DSC enthalpy measurements occurred in the center of a heating cycle. The measured enthalpies during those particular heating cycles contained the enthalpy of fusion plus enthalpies for raising the solid from the initial temperature to the melting point and for raising the liquid from the melting point to the final temperature. Details of derived enthalpies of fusion at the melting point are reported in Table 2. For pyrazine a phase transition at 300.5 K was noted during the measurements and the corresponding enthalpy (Table 2) was derived using a similar methodology to that outlined for the enthalpies of fusion.

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 4. The temperatures are precise to ±0.005 K. The expected accuracy of the densities is $\pm 0.1\ \mathrm{kg \cdot m^{-3}}$.[10]

Fitting Procedures. Pyrazine was the sole compound for which a critical temperature was measured. For that compound, a simultaneous nonlinear least-squares fit of the vapor pressures listed in Table 1 and the two-phase heat capacities $C_{\mathrm{x,m}}^{\mathrm{II}}$ given in Table 2 was completed. The fitting procedure has been described in detail by Steele,[9] and hence, only a summary of the procedure follows.

The Wagner equation[4] in the formulation highlighted by Ambrose and Walton,[13]

$$\ln(p/p_{\mathrm{c}}) = (1/T_{\mathrm{r}})[AY + BY^{1.5} + CY^{2.5} + DY^{5}] \qquad (2)$$

where $T_{\mathrm{r}} = T/T_{\mathrm{c}}$ and $Y = (1 - T_{\mathrm{r}})$, was fitted to the measured vapor pressures (Table 1) using a critical temperature of 627 K and with the critical pressure, p_{c}, included in the variables. The vapor-pressure fitting procedure including the minimization equation and the relative weightings is detailed in ref 9.

For fitting the two-phase heat capacities obtained in a cell of volume V_x, the experimental $C_{\mathrm{x,m}}^{\mathrm{II}}$ values (Table 2) were converted to $C_{\mathrm{V,m}}^{\mathrm{II}}$ by means of eq 1 for the cell

Table 4. Measured Liquid-Phase Densities along the Saturation Line[a]

T/K	ρ/kg·m^{-3}	$100(\rho - \rho_{calc})/\rho$	T/K	ρ/kg·m^{-3}	$100(\rho - \rho_{calc})/\rho$
ϵ-Caprolactam[b]			Pyrazine[c]		
353.131	1012.8	0.00	333.296	1034.7	0.00
373.124	997.4	−0.01	348.153	1018.7	0.02
398.118	977.6	0.03	373.154	991.2	0.02
423.113	958.1	0.00	398.147	962.2	0.04
448.111	938.1	0.01	423.149	932.7	−0.06
473.111	918.4	−0.04	434.331	917.7	0.03
498.108	897.3	0.02	448.150	899.6	0.02
1,2-Propanediol[d]			Triethylene Glycol[e]		
323.136	1013.1	0.07	313.139	1107.1	0.04
348.130	992.5	−0.04	348.129	1079.7	−0.03
373.124	971.8	−0.08	373.121	1059.4	−0.08
398.117	951.2	−0.01	398.119	1040.1	0.02
423.115	929.4	−0.06	423.114	1020.0	0.13
448.150[f]	901.0	−0.44	448.111	996.1	−0.05
			473.111	973.4	−0.01
Phenyl Acetylene[g]			Diphenyl Acetylene[h]		
323.136	900.6		350.012	979.3	−0.03
348.130	876.8		373.120	964.3	0.02
373.126	860.0		398.120	947.9	0.02
			423.110	931.1	0.00
			448.110	913.9	−0.03
			473.110	896.3	−0.03
			498.108	878.3	0.04

[a] ρ_{calc} values were calculated using eq 7 and the parameters listed below. [b] $\rho_{calc} = 309.6 + 1013.8(1 - T/806)^{1/3} - 897.3(1 - T/806)^{2/3} + 850.0(1 - T/806)$. [c] $\rho_{calc} = 353.0 + 591.4(1 - T/627)^{1/3} + 334.5(1 - T/627)^{2/3} + 43.75(1 - T/627)$. [d] $\rho_{calc} = 308.0 + 747.0(1 - T/676)^{1/3} + 158.54(1 - T/676)^{2/3}$. [e] $\rho_{calc} = 304.0 + 650.8(1 - T/770)^{1/3} + 417.5(1 - T/770)^{2/3} - 65.67(1 - T/770)$. [f] Compound decomposition (see text). [g] Because of the short temperature range, no fit was attempted. [h] $\rho_{calc} = 300.0 + 2467.2(1 - T/860)^{1/3} - 3505.2(1 - T/860)^{2/3} + 2153.7(1 - T/860)$.

expansion and the vapor-pressure fit for $(\partial p/\partial T)_{sat}$,

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

The values of $C^{II}_{V,m}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{sat}$ and $(\partial^2 \mu/\partial T^2)_{sat}$ (see eq 2 of ref 9). The functional form chosen for variation of the second derivative of the chemical potential with temperature was

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

Details of the weighting procedures and so forth are given in ref 9.

In 1995 as part of a study for DIPPR Project 851, VonNiederhaurern et al.[14] measured a critical temperature of 676.4 K for 1,2-propanediol. Fitting procedures for 1,2-propanediol followed that for pyrazine using the VonNiederhaurern et al.[14] value for T_c.

For the remaining four compounds, estimates were made for the critical temperature using literature techniques such as those due to Joback[15] and Ambrose[16,17] 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 $C^{II}_{x,m}$ 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 $T_r = 0.85$ (ref 18). Application of this criterion was discussed recently by Steele.[9]

Derived Results. Table 5 listed 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 $\Delta p = p - p_{Wagner}$ with p_{Wagner} calculated using the parameters listed in Table 5).

Table 5. Parameters for Eq 2 and Eq 4, Critical Constants, and Acentric Factors[a]

ϵ-Caprolactam				Pyrazine			
A	−9.521 61			A	−7.971 94	b_0	−0.245 95
B	4.656 13			B	3.110 79	b_1	−0.416 62
C	−5.935 83			C	−3.238 85	b_2	0.380 25
D	−3.693 00			D	−2.763 41	b_3	−0.486 72
T_c	806	p_c	4800	T_c	627	p_c	6700
ρ_c	310	ω	0.4847	ρ_c	353	ω	0.2699
1,2-Propanediol				Triethylene Glycol			
A	−11.102 14	b_0	−0.333 07	A	−15.086 38		
B	7.169 23	b_1	−0.692 37	B	13.412 60		
C	−10.500 10	b_2	0.065 40	C	−14.673 10		
D	−0.544 95	b_3	0.351 31	D	1.289 63		
T_c	676.4	p_c	6750	T_c	770	p_c	4400
ρ_c	308	ω	0.6575	ρ_c	304	ω	0.8874
Phenyl Acetylene				Diphenylacetylene			
A	−8.471 90			A	−8.402 90		
B	4.685 50			B	2.587 20		
C	−5.467 26			C	−3.362 86		
D	−0.828 43			D	−4.522 20		
T_c	650	p_c	4760	T_c	860	p_c	4200
ρ_c	302	ω	0.2676	ρ_c	300	ω	0.4099

[a] See text for details of how the parameters listed in this table were derived.

Table 6. Values of $C_{sat,m}/R$ (R = 8.314 51 J·K^{-1}·mol^{-1})

T/K	$C_{sat,m}/R$	T/K	$C_{sat,m}/R$
Pyrazine		1,2-Propanediol	
360.0	17.1	300.0	23.0
380.0	17.6	320.0	24.2
400.0	18.2	340.0	25.3
420.0	18.7	360.0	26.3
440.0	19.2	380.0	27.2
460.0	19.7	400.0	28.0
480.0	20.2	420.0	28.8
500.0	20.8	440.0	29.4
520.0	21.5	460.0	30.1
540.0	22.2	480.0	30.6
560.0	23.3	500.0	31.1
580.0	24.9	520.0	31.5
		540.0	32.0
		560.0	32.4
		580.0	33.0
		600.0	33.9

Values of $C^{II}_{V,m}(\rho = \rho_{sat})$ were derived for both pyrazine and 1,2-propanediol from the parameters listed in Table 5, and corresponding $C_{sat,m}$ values were obtained using eq 6 of ref 9. The results for $C_{sat,m}/R$ are reported in Table 6. The estimated uncertainty in these values is 1%.

Enthalpies of vaporization $\Delta_l^g H_m$ were derived from the Wagner-equation parameters (Table 5) using the Clapeyron equation:

$$dp/dT = \Delta_l^g H_m/(T\Delta_l^g V_m) \tag{5}$$

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]

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

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

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

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 4 and/or in Table 5. 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] Chirico and Steele applied this formulation for third virial coefficients successfully in analyses of the thermodynamic properties of benzene and toluene.[10] 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 7. 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 8. 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]

Comparison with Literature Values. ε-Caprolactam. The DIPPR Project 801 Database[24] lists critical properties for ε-caprolactam (T_c = 806 K, p_c = 4770 kPa, and ρ_c = 318 kg·m^{-3}) which are estimates. Sample decomposition prevented measurement of critical properties in this research. Values of T_c = (806 ± 10) K, p_c = (4800 ± 500) kPa, and ρ_c = (310 ± 20) kg·m^{-3} were used in this research.

As noted above, extensive decomposition occurred above 550 K during the vapor-pressure 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 ~530 K.

Figure 3A compares the Project 801 Database[24] correlation equation and vapor-pressure measurements listed in the following references (Moravek,[25] Daubert et al.,[26] Kozyro et al.[27]) with values for the saturation vapor pressure of ε-caprolactam obtained using eq 2 and the parameters listed in Table 5. Agreement with the measurements of Daubert et al.[26] is within the error limit of 5% assigned to those measurements in the 801 Database (the tabulated vapor pressure at 361.47 °C, i.e., 447,330 Pa, is probably a typographical error and probably should read 557,330 Pa).

Table 7. 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}
ε-Caprolactam		Pyrazine	
298.15[b,c]	75.06 ± 0.52	298.15[b,c]	41.02 ± 0.13
300.0[b,c]	74.89 ± 0.50	300.0[b,c]	40.98 ± 0.13
320.0[b,c]	72.95 ± 0.40	320.0[b,c]	39.86 ± 0.12
340.0[b,c]	71.06 ± 0.33	340.0	38.75 ± 0.13
360.0	69.21 ± 0.30	360.0	37.64 ± 0.15
380.0	67.41 ± 0.27	380.0	36.51 ± 0.20
400.0	65.66 ± 0.25	400.0	35.34 ± 0.27
420.0	63.96 ± 0.23	420.0	34.13 ± 0.35
440.0	62.29 ± 0.22	440.0[b]	32.86 ± 0.47
460.0	60.65 ± 0.22	460.0[b]	31.50 ± 0.60
480.0	59.02 ± 0.23	480.0[b]	30.07 ± 0.76
500.0	57.39 ± 0.25		
520.0	55.74 ± 0.32		
540.0	54.07 ± 0.40		
560.0	52.36 ± 0.50		
580.0[b]	50.59 ± 0.63		
600.0[b]	48.77 ± 0.80		
620.0[b]	46.9 ± 1.0		
1,2-Propanediol		Triethylene Glycol	
298.15[b]	67.49 ± 0.35	298.15[b]	84.6 ± 1.0
300.0[b]	67.32 ± 0.35	380.0[b]	77.69 ± 0.38
320.0[b]	65.53 ± 0.33	400.0[b]	75.89 ± 0.35
340.0[b]	63.72 ± 0.28	420.0[b]	74.06 ± 0.33
360.0[b]	61.88 ± 0.27	440.0	72.20 ± 0.30
380.0	60.02 ± 0.25	460.0	70.33 ± 0.28
400.0	58.12 ± 0.23	480.0	68.45 ± 0.28
420.0	56.16 ± 0.23	500.0	66.54 ± 0.28
440.0	54.13 ± 0.27	520.0	64.62 ± 0.32
460.0	52.02 ± 0.33	540.0	62.70 ± 0.38
480.0	49.81 ± 0.45	560.0	60.77 ± 0.48
500.0	47.51 ± 0.60	580.0[b]	58.85 ± 0.62
520.0[b]	45.11 ± 0.78	600.0[b]	56.94 ± 0.80
540.0[b]	42.6 ± 1.0		
560.0[b]	40.0 ± 1.3		
Phenyl Acetylene		Diphenyl Acetylene	
280.0[b]	44.71 ± 0.15	298.15[b,c]	75.9 ± 3.1
298.15[b]	43.78 ± 0.13	400.0[b]	66.91 ± 0.25
300.0[b]	43.68 ± 0.13	420.0[b]	65.33 ± 0.23
320.0	42.64 ± 0.13	440.0	63.81 ± 0.22
340.0	41.56 ± 0.13	460.0	62.33 ± 0.22
360.0	40.44 ± 0.13	480.0	60.89 ± 0.22
380.0	39.27 ± 0.17	500.0	59.47 ± 0.22
400.0	38.03 ± 0.22	520.0	58.06 ± 0.25
420.0[b]	36.72 ± 0.30	540.0[b]	56.65 ± 0.30
440.0[b]	35.34 ± 0.40	560.0[b]	55.21 ± 0.40
460.0[b]	33.88 ± 0.52	580.0[b]	53.74 ± 0.53

[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. [c] This temperature was below the melting point, and hence, the enthalpy value is for the hypothetical metastable liquid phase.

A detailed thermodynamic study of ε-caprolactam, including measurements of heat capacity in the temperature range 5 K to 550 K, sublimation pressures in the range 300 K to 340.2 K, an enthalpy of sublimation at 338.2 K, and energy of combustion, and a vibration spectral assignment have been reported by Kabo et al.[28]

The "third-law" method was employed to calculate sublimation pressures for ε-caprolactam from T = 290 K to the triple-point temperature (342.3 K). The "third-law" values were calculated from the tabulated entropies and enthalpies for the crystalline solid and the liquid (Table 2 of ref 28) and from extrapolated vapor pressures for the liquid phase calculated with the Wagner parameters listed

Table 8. Solubility Parameters δ^{a-c}

compound	ρ/mol·m^{-3}	$\Delta_l^g U_m$/J·mol^{-1}	$10^{-4}\delta$/(J·m^{-3})$^{1/2}$
ϵ-caprolactam	9024	67 900	2.48
pyrazine	13020	36 830	2.19
1,2-propanediol	13549	65 020	2.97
triethylene glycol	7442	82 120	2.47
phenyl acetylene	9037	42 230	1.95
diphenyl acetylene	6650	69 680	2.15

[a] Densities at 298.15 K or at the melting point if a solid 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 or, in the cases of ϵ-caprolactam, pyrazine, and diphenyl acetylene, at the melting point. [c] The melting point of ϵ-caprolactam was 342.3 K. The melting point of pyrazine was 325.5 K. The melting point of diphenyl acetylene was 335 K.

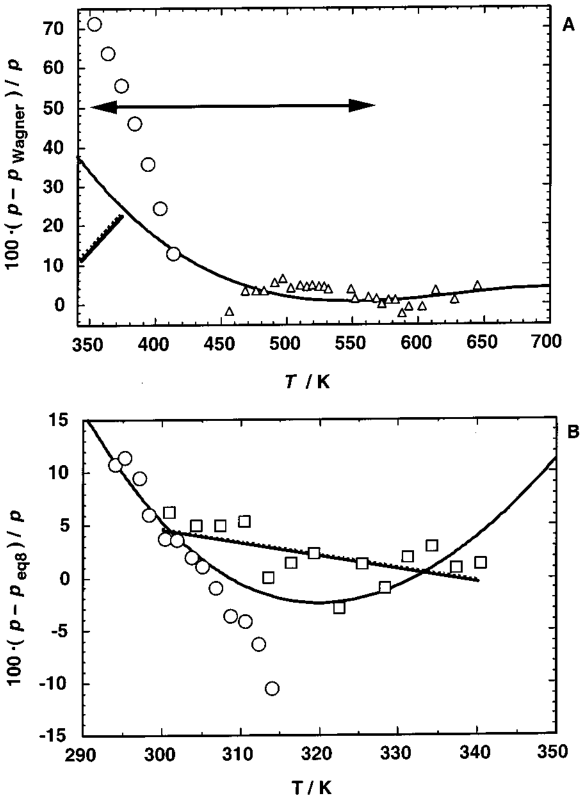

Figure 3. (A) Comparison of literature saturation vapor pressures for ϵ-caprolactam with values obtained using the Wagner equation (eq 2) and the parameters listed in Table 5. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (see Table 1). The solid line represents the deviations obtained using the DIPPR 801 Project Database[24] correlation equation. The dashed line represents the deviations from the equation listed in Table 2 of ref 27. Key: (○) Moravek;[25] (△) Daubert et al.[26] (B) Comparison of literature sublimation vapor pressures for ϵ-caprolactam with values obtained using eq 8. The solid line represents the deviations obtained using the DIPPR 801 Project Database[24] correlation equation. The dashed line represents the deviations from the equation listed in Table 2 of ref 27. Key: (○) Aihara;[31] (□) Kabo et al.[28] Not shown is a representation of the equation due to Hoyer and Peperle;[32] see text.

Table 9. Comparison of Enthalpies of Sublimation or Vaporization Found in a Search of the Literature with Values Derived in This Research

ϵ-Caprolactam

ref	$\Delta_{cr}^g H_m$/kJ·mol^{-1}	T/K	Δ^a/kJ·mol^{-1}
32	77.4	283	−11.7
31	83.09	304	−5.3
28	89.30 ± 0.81	320	1.4
	86.80 ± 0.22	320	−1.1
	86.30 ± 0.22	338.4	−0.9
	89.76 ± 0.81	298.15	1.2

1,2-Propanediol

ref	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	Δ^a/kJ·mol^{-1}
43	66.7	313	0.5
	65.4	333	1.0
	64.2	353	1.7
	62.6	373	1.9
	60.9	393	2.1
	59.7	413	2.9
	57.7	433	2.9
	55.5	453	2.7
	54.5	460	2.5

Diphenyl Acetylene

ref	$\Delta^g_{cr}H_m$/kJ·mol^{-1}	T/K	Δ^a/kJ·mol^{-1}
63	91.0 ± 4.6	298.15	−4.7
62	95.1 ± 1.1	298.15	−0.6

[a] $\Delta = \Delta_{cr}^g H_m$(ref) − $\Delta_{cr}^g H_m$(this research) in units of kJ·mol^{-1}.

in Table 5. The method employed was used previously[29,30] for biphenyl and naphthalene. The sublimation pressures for ϵ-caprolactam were represented by the equation

$$\ln(p/p°) = 26.1192 - (2.9567 \times 10^3)(T/\mathrm{K})^{-1} - (2.3254 \times 10^6)(T/\mathrm{K})^{-2} + (2.2604 \times 10^8)(T/\mathrm{K})^{-3} \quad (8)$$

in the temperature region 290 K to 342.3 K, with $p° = 1$ Pa. Figure 3B shows the deviations of values calculated using eq 8 from the Knudsen effusion measurements reported by Aihara,[31] Kozyro et al.,[27] and Kabo et al.[28] and from the Project 801 Database[24] sublimation vapor-pressure correlation equation. Agreement with both the 1989 and the 1992 results[27,28] is excellent, showing that the liquid-phase vapor-pressure measurements reported here are thermodynamically consistent with the Russian thermodynamic property measurements. Not shown in Figure 3B are the results of Hoyer and Peperle,[32] who report an equation for the sublimation pressure in the temperature region 258 K to 308 K obtained using the Knudsen effusion technique. Over the region of overlap (290 K to 308 K), the results of Hoyer and Peperle[32] are 9% to 34% low relative to those calculated using eq 8.

Only single-temperature point values for the density of ϵ-caprolactam were found in a search of the literature through June 1997. Over the temperature range of the measurements (Table 4), the DIPPR Project 801 Database[24] correlation equation gives values of the saturation density which are on average 4 kg·m^{-3} (0.4%) greater than those reported.

The saturation heat capacities, $C_{sat,m}$, reported in Table 2 are in excellent agreement with those listed in Table 2 of ref 28. The derived enthalpy of fusion $\Delta_{cr}^l H_m$(ϵ-caprolactam, 342.3 K) = (16.2 ± 0.3) kJ mol^{-1} is in excellent agreement with values of 16.1 kJ mol^{-1} (ref 33); (16.09 ± 0.03) kJ mol^{-1} (ref 34); and 16.1 kJ mol^{-1} (ref 28). Several enthalpies of sublimation $\Delta_{cr}^g H_m$ for ϵ-caprolactam have been reported[28,31,32] (see Table 9). Agreement with values derived in this research (see column 4 of Table 9) is within the probable combined uncertainty intervals.

Pyrazine. In the research reported here, values of T_c = 627 K and ρ_c = 353 kg·m^{-3} were determined from the DSC measurements and p_c = 6700 kPa was derived using the fitting procedures (see Figure 2 and Table 5). A search of the literature through June 1997 failed to find any papers

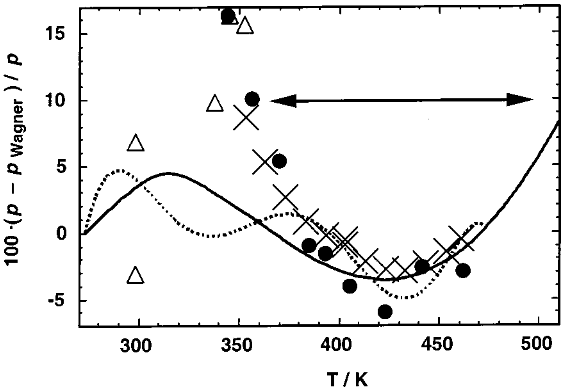

Figure 4. Comparison of literature saturation vapor pressures for 1,2-propanediol with values obtained using the Wagner equation (eq 2) and the parameters listed in Table 5. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (see Table 1). The solid line represents the deviations obtained using the DIPPR 801 Project Database.[24] The dashed line represents the deviations obtained using the vapor pressures reported in the review by Jones and Tamplin.[43] Key: (×) Schierholtz and Staples;[40] (△) Puck and Wise;[41] (●) Stull.[42]

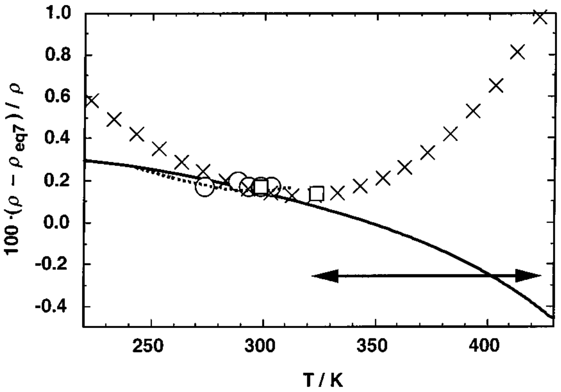

Figure 5. Comparison of literature saturation liquid densities for 1,2-propanediol with values obtained using eq 7 and the parameters listed in footnote *d* to Table 4. The double-headed arrow represents the temperature span of the density measurements obtained in this research (see Table 4). The solid line represents the deviations obtained using the DIPPR 801 Project Database.[24] The dashed line represents the deviations obtained using densities reported in the review by Jones and Tamplin.[43] Key: (□) Smyth and Walls;[44] (○) Timmermans and Hennaut-Roland;[45] (×) Zhuravlev et al.[46]

detailing experimental measurements of the critical properties or saturation liquid-phase densities over a range of temperature for pyrazine. In addition to a paper reporting saturated vapor pressures,[35] the only detailed thermophysical properties reported relate to the measurement of the enthalpies associated with phase transitions in pyrazine[36−38] and to its energy of combustion.[39]

With the exception of one listed point (332.44 K/13.79 kPa), the vapor pressures obtained by Sakoguchi et al.[35] are in good agreement (±1%) with values obtained using eq 2 and the parameters listed in Table 5. At 332.44 K the pressure obtained using eq 2 and the parameters listed in Table 5 is 13.37 kPa (3% lower).

The phase transition measurements of Schettino et al.,[36] Bougeard et al.,[37] and Boyd et al.[38] all agree on a transition at 300.65 K and point to a second one at 310 K. Boyd et al.[38] measured values of 976 J·mol^{-1} and 963 J·mol^{-1} for the transition at 300.65 K which can be compared with the value $\Delta_{\mathrm{cII}}^{\mathrm{cI}}H_{\mathrm{m}}^{\circ}(300.5\ \mathrm{K}) = (0.9 \pm 0.1)$ kJ mol^{-1} obtained in this research. The transition at 310 K was shown by Boyd et al. to have a small excess energy, (60 ± 10) J·mol^{-1}. Such a small excess energy is not detectable with the differential scanning calorimeter used in our study.

1,2-Propanediol. Using the critical temperature of 676 K obtained by VonNiederhausern et al.,[14] in the DIPPR 851 Project for 1995 the fitting procedures resulted in derivation of a critical pressure of (6750 ± 500) kPa and a critical density of (308 ± 20) kg·m^{-3} for 1,2-propanediol. VonNiederhausern et al.[14] list a critical pressure of (5941 ± 7) kPa obtained via extrapolation of their measured values to "zero residence time." Their uncertainty interval of only 7 kPa seems very optimistic. Figure 4 compares literature values for the vapor pressure of 1,2-propanediol[40−43] and the DIPPR 801 Project Database[24] with values obtained using the Wagner equation (eq 2) and the parameters listed in Table 5. Agreement between the sets of measurements is good within the temperature range 370 K to 470 K.

Figure 5 compares ρ_{sat} values for 1,2-propanediol found in the literature[43−46] with values calculated using eq 7 and the parameters listed in the footnotes to Table 4.

Table 9 gives a comparison of enthalpies of vaporization for 1,2-propanediol found in the literature[43] with values derived in this research (Table 7). Jones and Tamplin[43] report that values for the enthalpy of vaporization were measured in the temperature range 358 K to 423 K. However, the corresponding table of results (their Table 9.7) lists just the values reported in Table 9 that they state "were taken from a line through the experimental points and the calculated value of 170 cal/g". The "170 cal/g" value was obtained for the enthalpy of vaporization at the normal boiling point. The differences (all less than 3 kJ·mol^{-1}) listed in column 4 of Table 9 are within the estimated overall probable errors in the measurements.

Triethylene Glycol. A literature search produced references to determinations of the vapor pressure,[26,42,47−52] heat capacity,[53] and density.[50,54,55]

Rapid decomposition in the region of the critical point prevented measurement of the critical temperature and density using the DSC method. Anselme and Teja[56] found a similar problem for diethylene glycol during their study of the critical properties of "rapidly reacting substances." They noted that the critical temperature of diethylene glycol is greater than 723.5 K and their partially filled ampules exploded when heated to that temperature. Recently Nikitin et al.[57] have studied the critical temperatures and pressures of several poly(ethylene glycol)s using a pulse-heating method. Nikitin et al. list a critical temperature of 797 K for triethylene glycol with a corresponding critical pressure of 3300 kPa. While that critical temperature is possibly "correct", in this research a value of 770 K (more in line with the value of 753 K for diethylene glycol given by Nikitin et al.[57]) is used and a corresponding critical pressure of 4400 kPa derived using the fitting procedures (see above).

Figure 6 compares the values of the vapor pressure of triethylene glycol obtained in the literature search with those obtained in this research (Table 1) or derived using the Wagner equation and the parameters listed in Table 5. Shown in the figures is a solid line representing the DIPPR 801 1996 version of the vapor-pressure equation[24] for triethylene glycol. Stull[42] lists values in his review of the vapor-pressure literature that reproduce the previous results of Gallaugher and Hibbert,[47] who noted that their sample decomposed above 480 K. The onset for decomposition for the sample used in the present research was above

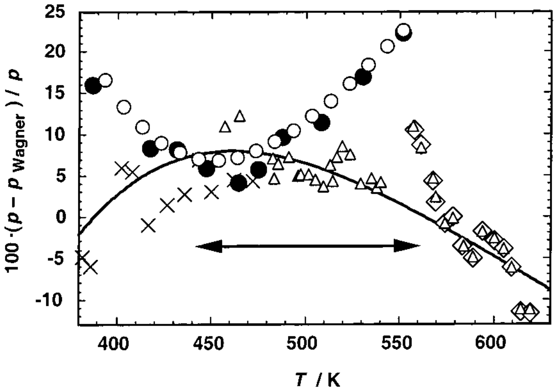

Figure 6. Comparison of literature vapor pressures for triethylene glycol with values obtained using the Wagner equation (eq 2) and the parameters listed in Table 5. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (see Table 1). The solid line represents the deviations obtained using the DIPPR 801 Project Database.[24] Key: (○) Gallaugher and Hibbert;[47] (●) Stull;[42] (◇) Lyons;[51] (△) Daubert et al.;[26] (×) Rowley and Hoffman.[52]

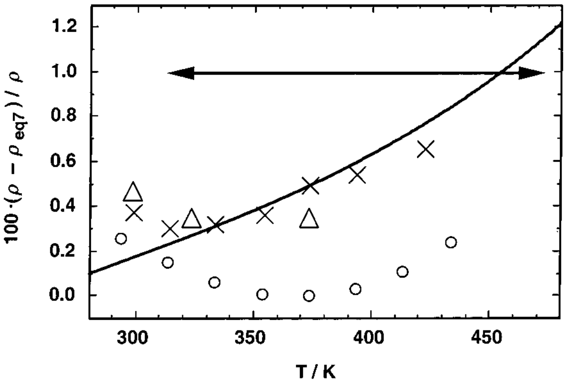

Figure 7. Comparison of literature saturation liquid densities for triethylene glycol with values obtained using eq 7 and the parameters listed in footnote *e* to Table 4. The double-headed arrow represents the temperature span of the density measurements obtained in this research (see Table 4). The solid line represents the deviations obtained using the DIPPR 801 Project Database.[24] Key: (○) Gallaugher and Hibbert;[54] (△) Brunner;[50] (×) Tawfik and Teja.[55]

560 K (>101 kPa). The thesis measurements of Lyons[51] are reproduced in the listed high-temperature measurements of Daubert et al.[26] The measurements of Daubert et al.[26] are approximately 5% lower than those obtained in this research across the region of overlap. The Daubert et al. results fall into two mutually incompatible groups: 482 K to 533 K and 583 K to 619 K. Sample decomposition could account for the incompatibilities. Not shown in Figure 6 are the measurements of Wise et al.,[48] Ishiguro and Matsumoto,[49] and Brunner.[50] The values reported in those three references are in the region of ambient temperature and differ from values derived by extrapolation using the Wagner equation and the parameters listed in Table 5 by ~60% on average. Because the extrapolation is so long (140 K), the comparison may have little meaning.

Figure 7 compares literature values for the saturation density of triethylene glycol with values obtained using eq 7 and the parameters listed in footnote *e* of Table 4. With the exception of the measurements of Gallaugher and Hibbert[54] in the temperature region 350 K to 400 K, all the densities reported in the literature are higher than those obtained in this research.

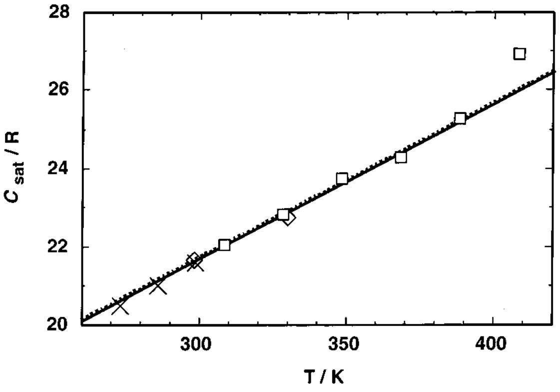

Figure 8. Comparison of saturation liquid-phase heat capacities for phenyl acetylene found in the literature search with values obtained using the equation listed in Table 2. The dashed line represents the equation. Key: (×) Smith and Andrews;[61] (◇) Lebedev et al.;[60] (□) the actual measured values for a cell containing 20 mg of sample.

Stephens and Tamplin obtained liquid-phase heat capacities for triethylene glycol.[53] Agreement between their results and values obtained using the saturation heat capacity equation given in Table 2 is poor and cannot be explained at present, since both were obtained using DSC. Stephens and Tamplin assign the change in slope of a plot (their Figure 3) at 441 K to decomposition which they compared to a decomposition temperature of 480 K obtained by Gallaugher and Hibbert,[54] during their vapor-pressure measurements. As noted above, no decomposition of the sample was found below 560 K during the measurements reported in this research.

Phenyl Acetylene. Onset of sample decomposition was noted in the ebulliometric vapor-pressure measurements for phenyl acetylene above 400 K. The thermal polymerization of phenyl acetylene is well documented in the literature, for example, Higashiura et al.[58] in the temperature range 403 K to 443 K under nitrogen and Yu-Ch'eng Liu et al.[59] between 423 K and 773 K. More recently, Lebedev et al.[60] have studied the thermodynamics of phenyl acetylene and its cyclotrimerization to 1,3,5-triphenylbenzene. Other than heat capacity measurements reported by Smith and Andrews[61] and Lebedev et al.,[60] no other thermophysical property measurements were found in a search of the literature through June 1997. Figure 8 compares saturation liquid-phase heat capacities for phenyl acetylene found in the literature search with values obtained using the equation listed in Table 2. Agreement between the sets of measurements is excellent.

The DIPPR Project 801 Database[24] lists critical properties for phenyl acetylene ($T_c = 650$ K, $p_c = 4280$ kPa, and $\rho_c = 308$ kg·m^{-3}) which are estimates. Accepting the critical temperature, the fitting procedures used in this research provide values of $p_c = (4760 \pm 500)$ kPa and $\rho_c = (302 \pm 20)$ kg·m^{-3}.

Diphenyl Acetylene. Although not up to the usual purity level obtained for samples within this Project, the thermophysical property measurements listed for diphenyl acetylene in the tables are probably sufficient for most property correlations. Sample decomposition prevented any measurements above 520 K. Other than heat capacity measurements reported by Smith and Andrews,[61] solid-phase effusion vapor-pressure measurements,[62] and two derived determinations of the enthalpy of sublimation at 298.15 K,[62,63] no other thermophysical property measurements were found in a search of the literature through June 1997.

Agreement between the heat capacity measurements reported by Smith and Andrews[61] and those derived using the equations listed in Table 2 is excellent (±1%). The enthalpy of sublimation values at 298.15 K are compared in Table 9. Agreement between the result of Diogo et al.[62] and that derived in this research, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(\mathrm{C_{14}H_{10}}, 298.15\ \mathrm{K}) = (95.7 \pm 3.1)\ \mathrm{kJ{\cdot}mol^{-1}}$, is nearly perfect.

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 ϵ-caprolactam at ~550 K during the ebulliometric vapor-pressure measurements with the possibility of initial decomposition at ~530 K. Applying that rule in this case leads to a bond dissociation energy in the range of 285 to 296 kJ·mol^{-1} for ϵ-caprolactam.

The decomposition temperatures for triethylene glycol (560 K), phenyl acetylene (400 K), and diphenyl acetylene (520 K) are all too low compared to known values for C−C bond dissociation energies to signify radical formation being the initial step in the decomposition reactions. In each case a concerted condensation reaction mechanism (see ref 64) is the probable initial pathway.

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