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Vapor Pressure, Heat Capacity, and Density along the Saturation Line, Measurements for Dimethyl Isophthalate, Dimethyl Carbonate, 1,3,5-Triethylbenzene, Pentafluorophenol, 4-*tert*-Butylcatechol, α-Methylstyrene, and *N*,*N*′-Bis(2-hydroxyethyl)ethylenediamine

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This paper reports measurements made for DIPPR Research Project 821 in the 1993 Project Year. Vapor pressures were measured to a pressure limit of 270 kPa or lower decomposition point for all seven compounds using a twin ebulliometric system and, for dimethyl isophthalate and *N*,*N*′-bis(2-hydroxyethyl)-ethylenediamine, additionally an inclined-piston apparatus. Liquid-phase densities along the saturation line were measured for each compound over a range of temperature (ambient to a maximum of 548 K). A differential scanning calorimeter (DSC) 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. Where possible, the critical temperature and critical density for each compound were determined experimentally. The results of the measurements were combined to derive a series of thermophysical properties including critical temperature, critical density, critical pressure, acentric factor, enthalpies of vaporization (restricted to within ±50 K of the temperature region of the experimentally determined 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 three-term $[(1 - T_r)^{1/3}]$ power series. All measured and derived values were compared with those obtained in a search of the literature. Recommended critical parameters are listed for each of the compounds studied. A “Rule-Of-Thumb” derived in the 1992 Project Year is used to estimate thermal decomposition temperatures by radical scission from a knowledge of the bond dissociation energy or vice versa.

Introduction

For over 40 years this laboratory has been at the forefront of technical development in the accurate and precise measurement of vapor pressures of pure compounds in the pressure range 0.01 kPa to 270 kPa and temperature range 100 K to 675 K. Details of the equipment used and recent innovations to extend the temperature range from 450 K to the present 675 K limit are given (Swietoslawski, 1945; Osborn and Douslin, 1966; Chirico et al., 1989b; Douslin and McCullough, 1963; Douslin and Osborn, 1965; Steele et al., 1988a). In the pressure range 0.01 kPa to 3.5 kPa, an inclined-piston gauge is used to make the vapor-pressure measurements. Twin ebulliometers are used in the pressure range 2 kPa to 270 kPa. The overlap region provides a check of the consistency of the methods. This is necessary in accurate and precise work since the inclined-piston is a static apparatus and, hence, the results are susceptible to the presence of dissolved gases in the sample.

The pressure in the ebulliometric apparatus is determined precisely by the condensation temperature of the standard substance (*n*-decane or water). The ebulliometric measurements are not susceptible to dissolved gases since they are removed in the refluxing operation of the equipment. The difference between the boiling and condensation temperatures for the substance under study is monitored continuously and is directly related to the purity of the sample. For thermally unstable compounds, the onset of sample decomposition is evidenced by a sharp rise in this difference. Impurities, resulting from decomposition, at levels as low as 0.1% can be readily detected.

A goal of this project is to determine the vapor-pressure up to the critical point or lower decomposition point. For many compounds the equipment available at NIPER cannot fulfill this goal directly. The construction of the twin ebulliometers with borosilicate glass sets the pressure limit at 270 kPa. The use of a metal ebulliometer [such as that used in Ambrose et al. (1990)] would enable measurements to the critical point, provided the presence of the metal surface did not catalyze sample decomposition. It is hoped to develop a metal twin-ebulliometric vapor-pressure apparatus at NIPER to make experimental measurements in the high-pressure region. However, because of the period of time required to make such measurements ($^1/_4$ h per temperature point), it is probable that most compounds of interest to DIPPR members would decompose appreciably before the critical region.

Using a DSC technique developed at NIPER and accurate vapor pressures in the region below 270 kPa, it has been shown (Steele et al., 1988b; Knipmeyer et al., 1989; Chirico et al., 1989a; Steele, 1995) that reliable critical pressures can be derived. At NIPER, one of the objectives of the research programs funded by the U.S. Department of Energy is the extension of temperature limits of the in-house apparatus. In the area of heat capacity measurements, this objective has been fulfilled by the development of the DSC technique [applicable to 950 K (Steele, 1995)] to measure heat capacities to within 20 K of the critical point (Steele et al., 1988b; Knipmeyer et al., 1989). Combination of the measured two-phase (liquid + vapor) heat capacities (obtained for a minimum of three cell

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fillings) and vapor-pressure data (measured within the inclined-piston and ebulliometric regions) has enabled estimation of the critical pressure for the substance under study. The fitting procedures used have been described (Steele et al., 1988b; Knipmeyer et al., 1989; Steele, 1995). In addition, where sample decomposition does not occur or is sufficiently slow, the DSC has been used to obtain the critical temperature and critical density by mapping the two-phase (liquid + vapor) to one-phase (fluid) conversion region.

Derivation of heat capacities along the saturation line requires an accurate knowledge of the liquid-phase density. Hence, a vibrating-tube densitometer capable of measurements from ambient to 548 K (the temperature limit of the thermostated bath used in the measurements) has been constructed at NIPER (Chirico et al., 1993). Results obtained from the densitometer measurements are included in the fitting procedures used to derive the thermophysical properties reported in this paper.

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 to 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 at NIPER 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 {the Wagner (1973) equation in the formulation highlighted by Ambrose and Walton (1989)

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

where $T_r = T/T_c$, and $Y = (1 - T_r)$ was used}; 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); to derive the Hildebrand solubility parameter (Hildebrand and Scott, 1962) 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 1993 Project Year for DIPPR Project 821. Common synonyms are listed for each compound name.

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 (Steele et al., 1996a−c) give detailed references to the experimental techniques and fitting procedures. Therefore, in this paper no details are given, and the reader is referred to Steele et al. (1996a−c) 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 compounds were purified at NIPER by repeated distillations using a spinning-band column. GLC analyses of the 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.

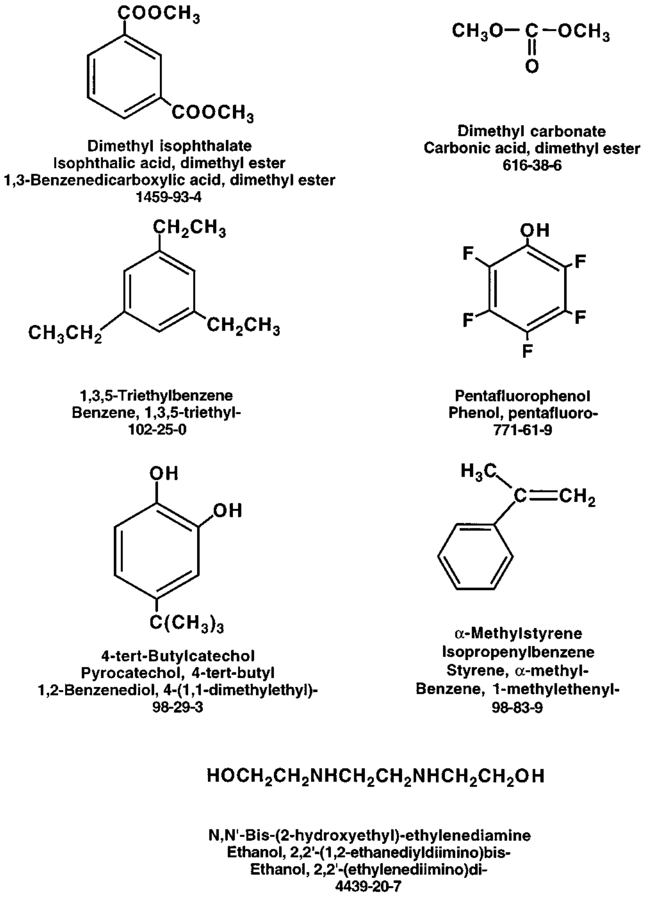

Figure 1. Structural formulas, common names, Chemical Abstract Service names (provided by the authors), and Chemical Abstract Services Registry Numbers (provided by the authors) for the compounds studied in this research.

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 (IUPAC, 1993) and the gas constant, $R = 8.314\,51$ J·K^{-1}·mol^{-1}, adopted by CODATA (Cohen and Taylor, 1988). 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 for Standards and Technology (NIST). All temperatures are reported in terms of ITS-90 (Goldberg and Weir, 1990; Mangum and Furukawa, 1990).

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
Dimethyl Isophthalate											
ip	349.981	0.0229	−0.0002	0.0002		d	495.089	19.930	0.001	0.001	0.016
ip	359.977	0.0460	0.0001	0.0002		d	502.880	25.051	0.000	0.001	0.013
ip	369.976	0.0873	0.0000	0.0002		w	502.828[b]	25.015	0.002	0.001	0.013
ip	379.976	0.1593	0.0000	0.0002		w	510.621	31.170	0.001	0.002	0.013
ip	389.972	0.2796	−0.0002	0.0002		w	518.446	38.553	0.000	0.002	0.012
ip	399.966	0.4748	0.0003	0.0003		w	526.324	47.369	−0.002	0.002	0.011
ip	409.969	0.7801	0.0002	0.0003		w	534.238	57.816	−0.002	0.003	0.012
ip	419.970	1.2452	0.0005	0.0004		w	542.185	70.109	−0.003	0.003	0.012
ip	429.961	1.9327	0.0001	0.0005		w	550.174	84.512	−0.002	0.004	0.012
d	430.830	2.0057	0.0001	0.0001	0.053	w	558.209	101.303	−0.003	0.004	0.011
ip	439.964	2.9296	0.0014	0.0007		w	566.286	120.78	0.00	0.00	0.013
d	447.830	3.9934	−0.0005	0.0002	0.039	w	574.393	143.20	0.00	0.01	0.013
d	455.451	5.3258	−0.0005	0.0003	0.033	w	582.562	169.03	0.00	0.01	0.015
d	466.780	7.9945	−0.0004	0.0004	0.022	w	590.744	198.46	0.00	0.01	0.018
d	475.242	10.658	0.000	0.001	0.018	w	598.976	232.02	0.01	0.01	0.025
d	482.045	13.306	0.000	0.001	0.017	w	607.225	269.95	−0.01	0.01	0.032
d	489.206	16.667	0.001	0.001	0.016						
Dimethyl Carbonate											
d	310.560	13.322	0.001	0.001	0.027	w	352.093	70.099	0.006	0.004	0.014
d	315.460	16.663	0.005	0.001	0.023	w	357.646	84.527	0.010	0.004	0.014
d	319.548	19.945	−0.002	0.001	0.020	w	363.240	101.348	0.004	0.005	0.013
d	324.866	25.009	−0.002	0.001	0.018	w	368.847	120.77	0.00	0.01	0.014
w	324.874[b]	25.018	−0.001	0.002	0.017	w	374.498	143.20	−0.01	0.01	0.012
w	330.257	31.177	0.000	0.002	0.016	w	380.197	169.01	−0.02	0.01	0.012
w	335.666	38.561	0.000	0.002	0.014	w	385.926	198.49	−0.01	0.01	0.012
w	341.113	47.374	−0.001	0.003	0.013	w	391.683	232.00	0.00	0.01	0.013
w	346.588	57.813	0.002	0.003	0.013	w	397.479	270.01	0.03	0.01	0.013
1,3,5-Triethylbenzene											
d	371.638	1.9984	0.0001	0.0001	0.050	w	459.329	47.370	−0.003	0.002	0.011
d	387.236	4.0010	0.0000	0.0002	0.029	w	466.654	57.809	−0.003	0.003	0.012
d	394.220	5.3408	−0.0006	0.0003	0.025	w	474.031	70.114	−0.002	0.003	0.012
d	404.498	7.9909	−0.0002	0.0004	0.019	w	481.446	84.508	−0.003	0.004	0.012
d	412.269	10.660	0.000	0.001	0.018	w	488.926	101.320	0.000	0.004	0.012
d	418.552	13.327	0.000	0.001	0.015	w	496.436	120.76	0.00	0.01	0.012
d	425.073	16.659	0.001	0.001	0.015	w	504.003	143.21	0.00	0.01	0.011
d	430.511	19.938	0.001	0.001	0.015	w	511.618	169.00	0.00	0.01	0.011
d	437.625	25.014	0.001	0.001	0.013	w	519.267	198.43	0.01	0.01	0.012
w	437.650[b]	25.034	0.002	0.001	0.012	w	526.972	231.96	0.00	0.01	0.012
w	444.821	31.177	0.001	0.002	0.012	w	534.724	269.99	−0.01	0.01	0.013
w	452.050	38.562	0.000	0.002	0.012						
Pentafluorophenol											
d	323.051	1.9989	−0.0004	0.0002	0.050	w	394.265	47.361	0.001	0.003	0.037
d	335.747	4.0021	0.0003	0.0003	0.050	w	400.214	57.815	−0.004	0.003	0.041
d	341.373	5.3288	0.0010	0.0004	0.050	w	406.191	70.113	−0.007	0.004	0.047
d	349.788	7.9947	0.0002	0.0005	0.048	w	412.206	84.531	0.003	0.004	0.054
d	356.071	10.651	0.001	0.001	0.045	w	418.258	101.316	0.009	0.005	0.055
d	361.183	13.320	−0.001	0.001	0.042	w	424.354	120.78	0.00	0.01	0.060
d	366.488	16.658	−0.001	0.001	0.038	w	430.481	143.21	0.01	0.01	0.060
d	370.855	19.901	0.000	0.001	0.037	w	436.655	168.99	0.02	0.01	0.062
d	376.682	25.020	−0.001	0.001	0.034	w	442.875	198.48	0.01	0.01	0.074
w	376.678[b]	25.017	−0.001	0.002	0.036	w	449.119	231.96	−0.01	0.01	0.079
w	382.508	31.175	0.001	0.002	0.032	w	455.414	269.98	−0.04	0.01	0.082
w	388.372	38.556	−0.007	0.002	0.037						
4-*tert*-Butylcatechol											
d	438.504	2.0038	0.0001	0.0001	0.122	d	488.397	13.313	0.000	0.001	0.053
d	445.105	2.6622	−0.0002	0.0002	0.108	d	495.365	16.662	0.001	0.001	0.046
d	455.064	4.0011	−0.0002	0.0002	0.097	d	501.127	19.933	−0.001	0.001	0.050
d	462.491	5.3380	0.0002	0.0003	0.088	d	508.675	25.012	−0.003	0.001	0.048
d	473.527	8.0089	−0.0001	0.0004	0.070	w	516.286	31.187	0.004	0.002	0.046
d	481.746	10.661	0.000	0.001	0.060						
α-Methylstyrene											
d	330.902	2.0020	0.0001	0.0001	0.020	w	404.598	38.566	0.000	0.002	0.011
d	345.094	3.9927	−0.0003	0.0003	0.017	w	411.285	47.366	−0.002	0.002	0.013
d	351.486	5.3305	−0.0001	0.0003	0.013	w	418.027	57.809	−0.001	0.003	0.014
d	360.967	7.9976	−0.0001	0.0005	0.013	w	424.810	70.098	−0.002	0.003	0.016
d	368.082	10.665	0.000	0.001	0.011	w	431.663	84.544	0.000	0.004	0.020
d	373.835	13.329	0.001	0.001	0.010	w	438.546	101.333	0.001	0.005	0.026
d	379.828	16.666	0.000	0.001	0.011	w	445.484	120.82	0.00	0.01	0.038
d	384.790	19.926	0.000	0.001	0.009	w	452.455	143.23	0.00	0.01	0.049
d	391.349	25.021	0.000	0.001	0.009	w	459.489[c]	169.00	−0.03	0.01	0.079
w	391.355[b]	25.028	0.002	0.001	0.010	w	466.566[c]	198.42	−0.10	0.01	0.105
w	397.984	31.212	0.001	0.002	0.011						

Table 1 (Continued)

method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K	method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
				N,*N*′-Bis(2-hydroxyethyl)ethylenediamine[d]							
ip	399.473	0.0270	0.0000	0.0001		ip	460.150	0.9155	0.0000	0.0002	
ip	410.150	0.0550	0.0000	0.0001		ip	470.150	1.4763	0.0000	0.0003	
ip	420.142	0.1029	0.0000	0.0001		ip	475.149	1.8581	0.0000	0.0004	
ip	430.151	0.1861	0.0000	0.0001		d	476.838	2.0057	0.0000	0.0001	0.074
ip	440.154	0.3258	0.0000	0.0001		d	492.718	3.9934	0.0001	0.0002	0.090
ip	450.151	0.5536	0.0000	0.0002		d	499.733	5.3258	−0.0001	0.0003	0.100

[a] Water (w) or 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 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 $\sigma(p) = (0.001)\ \{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{dT})^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\}^{1/2}$ (ebulliometer). ΔT is the difference between the boiling and condensation temperatures ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the sample. [b] Overlap point given zero weight in Wagner-equation fit to prevent bias in the fitting. [c] Point excluded from Wagner-equation fit due to sample decomposition (see text). [d] Due to the short temperature range of the measurements and the lack of reliable critical properties the results were fit to the Antoine vapor-pressure equation (see text). Then $\Delta p = p - p_{\mathrm{Antoine}}$.

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 dimethyl isophthalate, dimethyl carbonate, 1,3,5-triethylbenzene, pentafluorophenol, 4-*tert*-butylcatechol, α-methylstyrene, and *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine 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.

Inclined-piston vapor-pressure measurements for dimethyl isophthalate and *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine are also listed in Table 1. For these compounds the inclined-piston values extend the range of measured values down to 349 K and 399 K, respectively, close to the corresponding melting points (341.5 K and 373.15 K).

The difference between the boiling and condensation temperatures (ΔT) for 4-*tert*-butylcatechol increased by several tenths of a kelvin above 516 K. An attempt was made to make a measurement at 38.6 kPa (524 K), but ΔT started at approximately 0.05 K and rapidly increased by three-tenths of a kelvin. This phenomenon is normally indicative of sample decomposition. Sample decomposition was also noted in the DSC measurements, but only above 600 K (see Table 2).

For α-methylstyrene, sample decomposition (polymerization) started to occur significantly at 459.5 K (169 kPa) (see Table 1).

N,*N*′-Bis(2-hydroxyethyl)ethylenediamine also decomposed during the ebulliometric measurements. At 509 K (8 kPa) the value of ΔT started at approximately 0.1 K and rapidly increased by several tenths of a kelvin.

Differential Scanning Calorimetry. Table 2 lists the two-phase heat capacities $C_{\mathrm{x,m}}^{\mathrm{II}}$ determined by DSC for dimethyl isophthalate, dimethyl carbonate, 1,3,5-triethylbenzene, pentafluorophenol, 4-*tert*-butylcatechol, α-methylstyrene, and *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine for the given cell fillings. 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 energy additions. For each compound the upper temperature bound of the measurements was set by the critical region or earlier sample decomposition.

For dimethyl isophthalate, pentafluorophenol, 4-*tert*-butylcatechol, α-methylstyrene, and *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine extensive sample decomposition precluded attainment of heat-capacity measurements above the highest listed temperatures.

For dimethyl carbonate and 1,3,5-triethylbenzene measurements in the critical region were possible. For both of those compounds an abrupt decrease in the heat capacity associated with the conversion from two phases to one phase was observed. In each case sample decomposition was greatly reduced by employing a single continuous heat at a heating rate of 0.333 K·s^{-1}. Temperatures at which conversion to the single phase occurred were measured for each compound. Table 3 reports the density, obtained from the mass of sample and the cell volume calculated with the equation

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

where $y = (T - 298.15)$ K, $a = 3.216 \times 10^{-5}$ K^{-1}, and $b = 5.4 \times 10^{-8}$ K^{-2}, and the measured temperature at which conversion to a single phase was observed.

Critical temperatures and critical densities were derived graphically for both dimethyl carbonate and 1,3,5-triethylbenzene, as seen in Figure 2. Results of measurements on benzene and toluene performed as "proof-of-concept measurements" for these procedures have been reported (Chirico and Steele, 1994). The rapid heating method was used previously for critical temperature and critical density determinations for 2-aminobiphenyl (Steele et al., 1991), dibenzothiophene (Chirico et al., 1991), and carbazole, phenanthrene, and benzofuran (Steele, 1995).

For the compounds that were solid at 298.15 K, dimethyl isophthalate, 4-*tert*-butylcatechol, and *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, by judicious choice of starting temperature, 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 the derived enthalpies of fusion for dimethyl isophthalate, 4-*tert*-butylcatechol, and *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, at their melting points, and the corresponding values at 298.15 K are reported in Table 2. Equations, representing the heat capacities for the liquid and solid phases for each compound, which were used in the "adjustment" to 298.15 K, are also reported 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. Two-Phase (Solid + Vapor) or (Liquid + Vapor) Heat Capacities and Enthalpies of Fusion (R = 8.314 51 J·K^{-1}·mol^{-1})[a]

T/K	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$	T/K	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$
Dimethyl Isophthalate							
mass/g	0.010 061	0.019 534	0.024 241	vol cell/(cm^3)	0.053 39	0.052 72	0.053 39
355.0	39.4	39.5	40.1	535.0	51.5	50.0	49.9
375.0	40.8	40.1	41.1	555.0	53.0	51.5	50.8
395.0	42.4	41.0	42.3	575.0	54.0	53.3	52.2
415.0	43.6	42.1	43.4	595.0	56.2	55.0	53.7
435.0	44.9	43.1	44.2	615.0	58.7	56.8	54.5
455.0	46.9	44.7	45.7	635.0	61.1	58.7	55.5
475.0	47.4	45.9	47.0	655.0	62.8	60.0	56.7
495.0	48.9	47.4	48.0	675.0	65.8	62.4	58.5
515.0	50.1	48.3	48.8	695.0	68.7	66.6	60.0
crystalline $C_{\mathrm{sat,m}}/R = 0.1488T - 15.85$ (in temperature range 290 to 341.5 K)							
liquid $C_{\mathrm{sat,m}}/R = 0.059T + 18.58$ (in temperature range 341.5 to 420 K)							
$\Delta_{\mathrm{c}}^{\mathrm{l}}H^{\circ}_{\mathrm{m}}(341.5\ \mathrm{K}) = (30.15 \pm 0.4)$ kJ mol^{-1}				$\Delta_{\mathrm{c}}^{\mathrm{l}}H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K}) = (28.1 \pm 0.6)$ kJ mol^{-1}			
1,3,5-Triethylbenzene							
mass/g	0.009 377	0.014 966	0.021 050	vol cell/(cm^3)	0.052 72	0.053 39	0.053 39
315.0	36.6	36.6	36.9	515.0	53.1	52.5	51.8
335.0	38.6	38.1	38.4	535.0	56.1	54.2	53.1
355.0	39.9	39.3	39.7	555.0	57.9	56.0	54.6
375.0	41.5	40.6	41.3	575.0	60.5	57.5	56.3
395.0	43.5	42.5	42.5	595.0	62.9	59.4	57.8
415.0	44.8	44.1	44.3	615.0	65.2	61.2	59.4
435.0	45.7	45.8	45.8	635.0	68.7	63.4	61.8
455.0	47.7	47.3	47.5	655.0	72.5	67.0	63.2
475.0	49.8	48.9	49.0	675.0[b]	68.9	69.9	53.1
495.0	51.2	50.5	50.3				
Dimethyl Carbonate							
mass/g	0.011 118	0.015 826	0.021 424	vol cell/(cm^3)	0.052 72	0.053 39	0.053 39
315.0	20.9	20.3	20.1	455.0	28.9	26.5	25.3
335.0	21.2	20.9	20.7	475.0	30.8	27.6	26.3
355.0	22.1	21.7	21.3	495.0	33.2	29.6	27.5
375.0	23.8	22.5	22.1	515.0	35.5	31.1	28.9
395.0	24.9	23.5	22.9	535.0	39.1	33.8	30.8
415.0	25.9	24.5	23.6	555.0[b]	25.3	33.1	29.6
435.0	27.2	25.7	24.5				
Pentafluorophenol							
mass/g	0.012 580	0.018 792	0.026 454	vol cell/(cm^3)	0.054 48	0.053 39	0.053 39
330.0	33.7	33.6	33.6	470.0	40.1	37.9	36.7
350.0	33.8	33.6	33.5	490.0	42.0	39.2	37.7
370.0	34.2	33.8	33.7	510.0	44.0	40.5	38.6
390.0	34.8	34.3	34.0	530.0	46.3	42.0	39.6
410.0	35.7	34.9	34.4	550.0	49.0	43.6	40.6
430.0	36.9	35.7	35.1	570.0	52.7	45.7	41.8
450.0	38.4	36.8	35.9				
4-*tert*-Butylcatechol[c]							
350.0	45.3	490.0	51.7	430.0	48.8	570.0	54.5
370.0	46.3	510.0	52.4	450.0	49.8	590.0	55.6
390.0	47.5	530.0	53.2	470.0	50.9	610.0[b]	59.5
410.0	48.4	550.0	53.7				
crystalline $C_{\mathrm{sat,m}}/R = 0.020T + 36.1$ (in temperature range 290 to 327 K)							
liquid $C_{\mathrm{sat,m}}/R = 0.0526T + 26.87$ (in temperature range 327 to 410 K)							
$\Delta_{\mathrm{c}}^{\mathrm{l}}H^{\circ}_{\mathrm{m}}(327\ \mathrm{K}) = (4.5 \pm 0.2)$ kJ mol^{-1}				$\Delta_{\mathrm{c}}^{\mathrm{l}}H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K}) = (4.3 \pm 0.4)$ kJ mol^{-1}			
α-Methylstyrene							
mass/g	0.009 367	0.017 591	0.021 463	vol cell/(cm^3)	0.054 48	0.053 39	0.054 78
315.0	25.6	25.6	25.6	455.0	34.3	33.2	33.0
335.0	26.7	26.6	26.6	475.0	35.9	34.3	34.0
355.0	27.8	27.6	27.6	495.0	37.4	35.4	35.1
375.0	28.9	28.7	28.7	515.0	39.0	36.5	36.0
395.0	30.2	29.8	29.7	535.0	40.8	37.5	37.0
415.0	31.5	30.9	30.8	555.0	42.6	38.6	37.9
435.0	32.9	32.0	31.9	575.0	44.9	39.7	38.8
N,*N*′-Bis(2-hydroxyethyl)ethylenediamine[d]							
Crystalline							
315.0	26.9	335.0	28.9				
Liquid							
395.0	50.7	455.0	55.1	435.0	53.7		
415.0	52.1	475.0	56.3				
crystalline $C_{\mathrm{sat,m}}/R = 0.100T - 4.60$ (in temperature range 290 to 373.2 K)							
liquid $C_{\mathrm{sat,m}}/R = 0.071T + 22.70$ (in temperature range 373.2 to 485 K)							
$\Delta_{\mathrm{c}}^{\mathrm{l}}H^{\circ}_{\mathrm{m}}(373.2\ \mathrm{K}) = (49.7 \pm 0.5)$ kJ mol^{-1}				$\Delta_{\mathrm{c}}^{\mathrm{l}}H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K}) = (38.7 \pm 0.8)$ kJ mol^{-1}			

[a] Volume of cell (vol cell) is given for 298.15 K. [b] Values not used in fitting procedures since above either the critical or decomposition temperature. [c] Values were obtained with 0.019 506 g sample in a cell of volume 0.054 48 cm^3. Compound decomposed before difference between $C^{\mathrm{II}}_{\mathrm{x,m}}/R$ and $C_{\mathrm{sat,m}}/R$ became significant. [d] Values were obtained with 0.022 505 g sample in a cell of volume 0.054 48 cm^3. Compound decomposed before difference between $C^{\mathrm{II}}_{\mathrm{x,m}}/R$ and $C_{\mathrm{sat,m}}/R$ became significant.

Table 3. Densities and Temperatures Used To Define the Two-Phase Dome near T_c

ρ/(kg·m^{-3})	T/K
1,3,5-Triethylbenzene	
141.1	667.5
174.4	674.2
238.3	676.9
274.8	678.8
360.3	675.3
386.8	668.3
Dimethyl Carbonate	
140.4	540.1
208.4	552.4
236.9	552.6
292.9	556.3
325.7	556.6
396.6	555.6

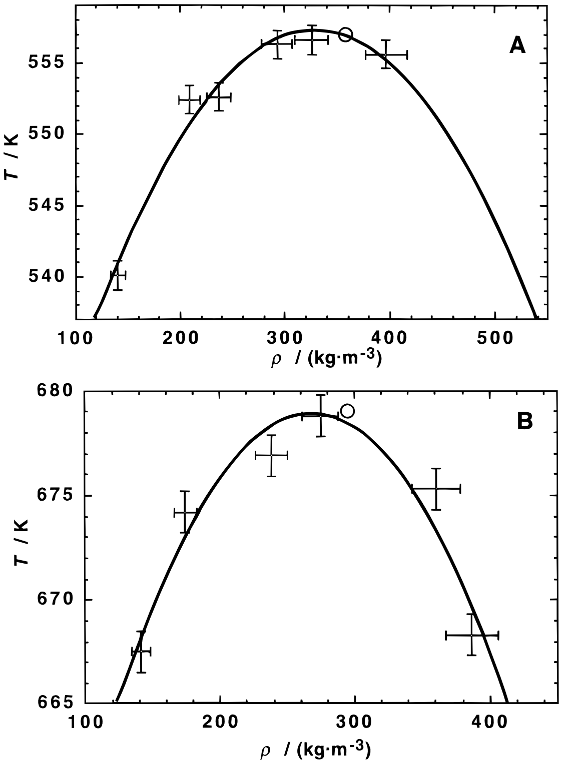

Figure 2. Vapor−liquid coexistence in the region of the critical point; A = dimethyl carbonate, B = 1,3,5-triethylbenzene. ○ denotes the critical temperatures and critical densities derived in the fitting procedures. The curves are drawn as an aid to the eye and do not represent any theoretically valid equation. The crosses span the range of uncertainty.

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

T/K	ρ/(kg·m^{-3})	$100(\rho - \rho_{\mathrm{calc}})/\rho$
Dimethyl Isophthalate[b]		
353.129	1148.4	−0.05
373.123	1130.2	0.06
398.118	1105.4	0.06
423.113	1078.8	−0.07
448.111	1053.0	−0.08
473.111	1027.2	−0.01
498.111	1000.9	0.06
523.109	973.1	0.07
548.110	942.8	−0.06
Dimethyl Carbonate[c]		
308.141	1049.6	0.00
323.137	1029.6	0.01
348.130	995.1	0.01
373.123	959.3	−0.02
393.119	930.2	0.01
1,3,5-Triethylbenzene[d]		
323.137	839.1	−0.05
348.130	819.5	0.02
373.123	799.4	0.09
398.119	778.3	0.07
423.115	755.2	−0.13
448.111	733.7	−0.06
473.111	711.8	0.08
Pentafluorophenol[e]		
323.136	1657.6	−0.07
348.130	1611.0	0.13
373.123	1557.5	0.00
398.118	1502.8	−0.08
423.113	1448.0	−0.01
448.118	1389.8	0.03
4-*tert*-Butylcatechol[f]		
348.130	1031.7	−0.04
373.122	1013.1	0.10
398.122	990.4	−0.11
423.113	970.4	0.03
α-Methylstyrene[g]		
323.138	886.6	−0.01
348.130	863.9	0.03
373.125	840.0	−0.06
398.119	817.5	0.04
423.115	793.4	−0.01
N,N'-Bis(2-hydroxyethyl)ethylenediamine[h]		
398.120	1014.6	
413.115	994.7	
448.115	974.2	

[a] ρ_{calc} values were calculated using eq 8 and the parameters listed below. [b] $\rho_{\mathrm{calc}} = 342.0 + 925.6(1 - T/766)^{1/3} - 429.8(1 - T/766)^{2/3} + 627.7(1 - T/766)$. [c] $\rho_{\mathrm{calc}} = 358.0 + 975.8(1 - T/557)^{1/3} - 715.1(1 - T/557)^{2/3} + 813.9(1 - T/557)$. [d] $\rho_{\mathrm{calc}} = 260.0 + 740.0(1 - T/679)^{1/3} - 478.9(1 - T/679)^{2/3} + 561.3(1 - T/679)$. [e] $\rho_{\mathrm{calc}} = 533.0 + 1181.5(1 - T/605)^{1/3} - 191.0(1 - T/605)^{2/3} + 697.0(1 - T/605)$. [f] $\rho_{\mathrm{calc}} = 297.0 + 498.1(1 - T/775)^{1/3} + 567.2(1 - T/775)^{2/3} - 98.6(1 - T/775)$. [g] $\rho_{\mathrm{calc}} = 288.0 + 1057.3(1 - T/645)^{1/3} - 1220.7(1 - T/645)^{2/3} + 1058.2(1 - T/645)$. [h] Due to short temperature range no fit was attempted.

Densitometry. Measured densities for dimethyl isophthalate, dimethyl carbonate, 1,3,5-triethylbenzene, pentafluorophenol, 4-*tert*-butylcatechol, α-methylstyrene, and *N,N'*-bis(2-hydroxyethyl)ethylenediamine in the liquid phase along the saturation line are listed in Table 4. The temperatures are precise to ±0.005 K. As derived (Chirico and Steele, 1994), the expected accuracy of the densities is ±0.1 kg·m^{-3}.

Fitting Procedures. With the exception of *N,N'*-(2-hydroxyethyl)ethylenediamine and 4-*tert*-butylcatechol, in general, the same fitting procedures were used for all the remaining compounds of this study. Details of the fitting procedures used for the diamine and the catechol are given at the end of this section. The fitting parameters were derived by 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. The Wagner equation (eq 1) was fitted to the measured vapor pressures (Table 7). The vapor-pressure fitting procedure including the minimization equation and the relative weightings is detailed in Steele (1995). In general, the number of fitting parameters differed depending on whether or not a critical temperature could be determined experimentally. For 1,3,5-triethylbenzene and dimethyl carbonate, critical temperatures were determined from the DSC measurements and, hence, only the critical pressure p_c was included in the variables. For the remaining compounds, extensive sample decomposition precluded critical temperature measurements and, therefore, both T_c and p_c were included as variables.

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 8) were converted to $C_{\mathrm{V,m}}^{\mathrm{II}}$ by means of eq 2 for the cell

Table 5. Parameters for Eqs 1 and 4, Critical Constants, and Acentric Factors[a]

	Dimethyl Isophthalate				Dimethyl Carbonate		
A	−10.178 84	b_0	−0.603 60	A	−8.242 79	b_0	−0.303 23
B	4.626 69	b_1	−0.562 12	B	3.255 66	b_1	−0.811 19
C	−6.969 76	b_2	0.311 60	C	−4.282 49	b_2	1.711 16
D	−2.776 45	b_3	−0.706 49	D	−2.119 40	b_3	−2.372 67
T_c	766 K	p_c	2650 kPa	T_c	557 K	p_c	4800 kPa
ρ_c	342 kg·m^{-3}	ω	0.6402	ρ_c	358 kg·m^{-3}	ω	0.3365
	1,3,5-Triethylbenzene				Pentafluorophenol		
A	−9.357 38	b_0	−0.654 16	A	−9.534 81	b_0	−0.355 45
B	3.788 30	b_1	−0.918 44	B	4.609 88	b_1	−1.657 36
C	−5.451 84	b_2	1.561 38	C	−6.431 14	b_2	3.933 71
D	−2.913 51	b_3	−1.763 57	D	−4.595 48	b_3	−5.820 98
T_c	679 K	p_c	2435 kPa	T_c	605 K	p_c	3800 kPa
ρ_c	260 kg·m^{-3}	ω	0.5266	ρ_c	533 kg·m^{-3}	ω	0.5083
	4-*tert*-Butylcatechol				α-Methylstyrene		
A	−10.869 60			A	−9.147 56	b_0	−0.396 92
B	3.247 82			B	4.487 77	b_1	−1.043 35
C	−1.763 64			C	−5.078 59	b_2	1.988 93
D	−15.953 72			D	−2.474 12	b_3	−1.980 14
T_c	775 K	p_c	3700 kPa	T_c	645 K	p_c	3550 kPa
ρ_c	297 kg·m^{-3}	ω	0.7700	ρ_c	288 kg·m^{-3}	ω	0.4041
	N,N′-Bis(2-Hydroxyethyl)ethylenediamine[b]						
A	8.239 2						
B	−3218.9						
C	−71.280						

[a] The parameters listed in this Table are those derived from the fitting procedures. [b] Antoine equation parameters listed here (see text and eq 5)

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

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

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 Steele (1995)]. The functional form chosen for variation of the second derivative of the chemical potential with temperature was

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

Details of the weighting procedures, etc., are given by Steele (1995).

Exceptions to the above procedures were made for both 4-*tert*-butylcatechol and *N,N′*-(2-hydroxyethyl)ethylenediamine. Both compounds decomposed well removed from the critical region, measured vapor pressures covered a relatively narrow range of temperature (Table 1), and the measured $C^{II}_{x,m}$ values (Table 2) were independent of cell filling.

For 4-*tert*-butylcatechol, an estimated critical temperature and pressure (775 K and 3700 kPa, respectively) were used in the fitting procedures. For *N,N′*-(2-hydroxyethyl)ethylenediamine, all estimating procedures gave unrealistic values for the critical parameters. Hence, for that compound, the Antoine equation in the form

$$\log(p/p_{ref}) = A + B/\{(T/\mathrm{K}) + C\} \quad (5)$$

with $p_{ref} = 1$ kPa, was fit to the available vapor-pressure data (Table 1).

Derived Results. Table 5 listed the parameters derived using the procedures outlined above and in Steele et al. (1996b). Details of the fits using to 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).

Values of $C^{II}_{x,m}(\rho = \rho_{sat})$ were derived from the parameters listed in Table 5, and corresponding $C_{sat,m}$ values were obtained using eq 6 of Steele et al. (1995). 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- or Antoine-equation fits (Table 5) using the Clapeyron equation

$$\mathrm{d}p/\mathrm{d}T = \Delta_l^g H_m/(T\,\Delta_l^g V_m) \quad (6)$$

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 (Riedel, 1954) as formulated by Hales and Townsend (1972)

$$(\rho/\rho_c) = 1.0 + 0.85Y + (1.6916 + 0.9846\omega)Y^{1/3} \quad (7)$$

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 7 was not a good representation of the measured densities. A power series of the type

$$\rho = \rho_c + A(1 - T_r)^{1/3} + B(1 - T_r)^{2/3} + C(1 - T_r) + \ldots \quad (8)$$

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 (Steele, 1996). Estimates of the liquid-phase volumes were made using eq 8 and the parameters given 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 (Pitzer and Curl, 1957), and third virial coefficients were estimated with the corresponding-states method (Orbey and Vera, 1983). This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene and toluene (Chirico and Steele, 1994). 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

Table 6. 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	$C_{\mathrm{sat,m}}/R$
	Dimethyl Isophthalate		
360.0	39.8	560.0	50.8
380.0	41.0	580.0	51.9
400.0	42.2	600.0	52.9
420.0	43.4	620.0	54.0
440.0	44.5	640.0	55.1
460.0	45.6	660.0	56.4
480.0	46.7	680.0	57.8
500.0	47.7	700.0	59.7
520.0	48.8	720.0	62.5
540.0	49.8	740.0	68.0
	Dimethyl Carbonate		
300.0	19.8	440.0	23.6
320.0	20.2	460.0	24.4
340.0	20.6	480.0	25.1
360.0	21.2	500.0	26.1
380.0	21.7	520.0	27.8
400.0	22.3	540.0	32.6
420.0	23.0		
	1,3,5-Triethylbenzene		
300.0	35.6	500.0	50.1
320.0	37.1	520.0	51.5
340.0	38.6	540.0	52.9
360.0	40.0	560.0	54.3
380.0	41.5	580.0	55.8
400.0	42.9	600.0	57.3
420.0	44.4	620.0	59.2
440.0	45.8	640.0	62.1
460.0	47.3	660.0	68.6
480.0	48.7		
	Pentafluorophenol		
320.0	33.6	460.0	34.7
340.0	33.4	480.0	35.3
360.0	33.4	500.0	35.8
380.0	33.4	520.0	36.5
400.0	33.6	540.0	37.2
420.0	33.9	560.0	38.5
440.0	34.3	580.0	42.6
	α-Methylstyrene		
300.0	24.9	480.0	33.6
320.0	25.8	500.0	34.5
340.0	26.8	520.0	35.4
360.0	27.8	540.0	36.2
380.0	28.8	560.0	37.0
400.0	29.8	580.0	38.1
420.0	30.8	600.0	39.7
440.0	31.8	620.0	43.6
460.0	32.7		

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.

The absence of critical properties precluded using the methodology outlined above for *N*,*N'*-bis(2-hydroxyethyl)ethylenediamine. For that compound, liquid-phase volumes were derived using the densities listed in Table 4 and an average coefficient of cubic expansion obtained from the measurements. Second virial coefficients were estimated with the correlation of Scott et al. (1950). Since enthalpies of vaporization were not derived for pressures greater than 1 bar, third virials were neglected. Uncertainties in both the liquid-phase molar volumes and virial coefficients were assumed to be 20% of the respective numerical values.

Solubility parameters are listed in Table 8.

Table 7. Enthalpies of Vaporization Obtained from the Wagner or Antoine and Clapeyron Equations[a]

T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}
	Dimethyl Isophthalate		
298.15[b]	77.17 ± 0.83	480.0	61.27 ± 0.45
300.0[b]	77.00 ± 0.83	500.0	59.52 ± 0.47
320.0[b]	75.15 ± 0.76	520.0	57.72 ± 0.50
340.0[b]	73.33 ± 0.72	540.0	55.83 ± 0.57
360.0	71.55 ± 0.67	560.0	53.86 ± 0.68
380.0	69.79 ± 0.62	580.0	51.78 ± 0.85
400.0	68.06 ± 0.57	600.0	49.6 ± 1.1
420.0	66.36 ± 0.53	620.0[b]	47.2 ± 1.3
440.0	64.67 ± 0.50	640.0[b]	44.7 ± 1.6
460.0	62.98 ± 0.47	660.0[b]	42.0 ± 1.9
	Dimethyl Carbonate		
280.0[b]	38.77 ± 0.25	380.0	32.41 ± 0.37
298.15[b]	37.70 ± 0.23	400.0	30.91 ± 0.50
300.0[b]	37.59 ± 0.23	420.0[b]	29.28 ± 0.65
320.0	36.38 ± 0.23	440.0[b]	27.54 ± 0.81
340.0	35.13 ± 0.25	460.0[b]	25.7 ± 1.0
360.0	33.82 ± 0.28		
	1,3,5-Triethylbenzene		
298.15[b]	59.22 ± 0.26	440.0	48.43 ± 0.18
300.0[b]	59.07 ± 0.26	460.0	46.82 ± 0.22
320.0[b]	57.49 ± 0.23	480.0	45.11 ± 0.26
340.0[b]	55.96 ± 0.22	500.0	43.31 ± 0.32
360.0[b]	54.45 ± 0.20	520.0	41.37 ± 0.42
380.0	52.97 ± 0.19	540.0[b]	39.29 ± 0.52
400.0	51.48 ± 0.17	560.0[b]	37.05 ± 0.63
420.0	49.98 ± 0.17	580.0[b]	34.60 ± 0.76
	Pentafluorophenol		
298.15[b]	52.21 ± 0.43	400.0	42.51 ± 0.35
300.0[b]	52.02 ± 0.43	420.0	40.61 ± 0.43
320.0[b]	50.04 ± 0.38	440.0[b]	38.65 ± 0.55
340.0	48.12 ± 0.35	460.0[b]	36.61 ± 0.70
360.0	46.25 ± 0.33	480.0[b]	34.48 ± 0.90
380.0	44.38 ± 0.32	500.0[b]	32.2 ± 1.1
	4-*tert*-Butylcatechol		
298.15[b]	96.5 ± 2.8	500.0	63.26 ± 0.47
400.0[b]	75.74 ± 0.70	520.0[b]	61.45 ± 0.48
420.0[b]	72.67 ± 0.62	540.0[b]	59.77 ± 0.53
440.0	69.92 ± 0.57	560.0[b]	58.17 ± 0.62
460.0	67.46 ± 0.52	580.0[b]	56.59 ± 0.75
480.0	65.24 ± 0.48		
	α-Methylstyrene		
290.0[b]	49.20 ± 0.37	400.0	41.97 ± 0.30
298.15[b]	48.64 ± 0.35	420.0	40.61 ± 0.33
300.0[b]	48.52 ± 0.35	440.0	39.19 ± 0.42
320.0[b]	47.19 ± 0.32	460.0	37.71 ± 0.53
340.0	45.89 ± 0.30	480.0[b]	36.14 ± 0.67
360.0	44.60 ± 0.28	500.0[b]	34.50 ± 0.83
380.0	43.29 ± 0.28	520.0[b]	32.8 ± 1.0
	N,*N'*-Bis(2-hydroxyethyl)ethylenediamine		
298.15[c]	106.4 ± 6.4	440.0	87.7 ± 0.2
300.0[c]	106.0 ± 6.4	460.0	86.2 ± 0.2
360.0[c]	95.8 ± 0.3	480.0	84.8 ± 0.2
380.0[c]	93.4 ± 0.3	500.0	83.5 ± 0.2
400.0	91.2 ± 0.2	520.0[c]	82.2 ± 0.3
420.0	89.4 ± 0.2		

[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] The value at this temperature was calculated with extrapolated vapor pressures derived from the fitted Antoine equation.

Discussion

General Comments. In this section emphasis is given to 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 DIPPR Project 801 (Daubert and Danner, 1993).

The experimentally determined values for the critical densities (obtained via the DSC method) have a relatively large uncertainty (±2.5%). For both 1,3,5-triethylbenzene and dimethyl carbonate the experimentally determined value range included the value derived in fitting the density measurements to extended corresponding states using eq 8.

Comparison with Literature Values. Dimethyl Isophthalate. With the exception of the results obtained by Kraus et al. (1962), vapor-pressure measurements for

Table 8. Solubility Parameters[a,b]

ρ/mol·m^{-3}	$\Delta_l^g U_m$/J·mol^{-1}	δ/(J·m^{-3})$^{1/2}$
	Dimethyl Isophthalate	
5976	70 328	2.05×10^4
	Dimethyl Carbonate	
11795	35 221	2.04×10^4
	1,3,5-Triethylbenzene	
5276	56 741	1.73×10^4
	Pentafluorophenol	
9128	48 436	2.10×10^4
	4-*tert*-Butylcatechol	
6251	87 941	2.35×10^4
	α-Methylstyrene	
7700	44 161	1.89×10^4
	N,*N*′-Bis(2-hydroxyethyl)ethylenediamine	
7169	91 070	2.56×10^4

[a] Densities (listed to an extra significant figure to prevent round off errors) were estimated by extrapolation of the third order fits listed in Table 4. [b] $\Delta_l^g U_m = (\Delta_l^g H_m - RT)$ obtained using the value for the enthalpy of vaporization at 298.15 K (or at the melting point if above 298.15 K) listed in Table 7. [c] Melting point dimethyl isophthalate 341.5 K, pentafluorophenol 310.56 K, 4-*tert*-butylcatechol 328.2 K, and *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine 373.2 K.

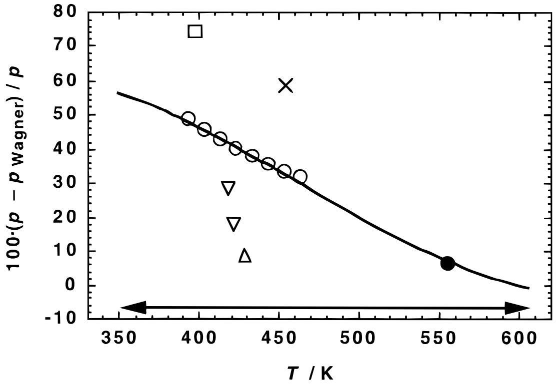

Figure 3. Comparison of literature vapor pressures for dimethyl isophthalate with those obtained using the Wagner equation and the parameters listed in Table 5. The double-headed arrow represents the range of the measurements of this research and reported in Table 1. The solid line represents deviations of the DIPPR Project 801 correlation (Daubert and Danner, 1993). Key: (□) Wegscheider et al. (1911); (○) Kraus et al. (1962); (●) Kucharenko and Grigor'eva (1970); (▽) DuPont (1970); (×) Bodnaryuk et al. (1972); (△) Murogova et al. (1974).

dimethyl isophthalate reported in the literature are restricted to single-point values obtained during preparation and purification of samples of the compound (Wegscheider et al., 1911; Du Pont, 1970; Kucharenko and Grigor'eva, 1970; Bodnaryuk et al., 1972; Murogova et al., 1974). All the available vapor-pressure values are compared in Figure 3. Also included in Figure 3 is a comparison of the DIPPR Project 801 (Daubert and Danner, 1993) correlated data with that obtained using the Wagner constants reported in this research (Table 5). It is apparent that the measurements of Kraus et al. (1962) and the normal boiling point of Kucharenko and Grigor'eva (1970) were used to derive the DIPPR Project 801 (Daubert and Danner, 1993) correlation for the vapor pressure of dimethyl isophthalate.

A search of the literature through January 1997 failed to produce any further thermophysical property measurements for dimethyl isophthalate. Except for a measured energy of combustion (Colomina et al., 1972), all other values listed by the DIPPR 801 Project for this compound are the result of correlations.

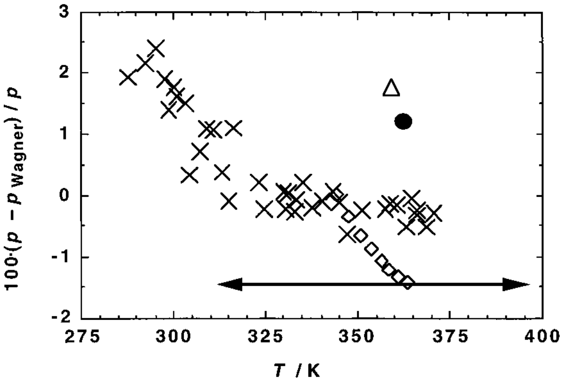

Figure 4. Comparison of literature vapor pressures for dimethyl carbonate with values obtained using the Wagner equation and the parameters listed in Table 5. The double-headed arrow represents the range of the measurements of this research and reported in Table 1. Key: (●) Vogel (1948); (◇) Wright (1960); (△) Cross et al. (1976); (×) Jiang and Zhang (1987).

Attempts to obtain a critical temperature value for dimethyl isophthalate using the DSC were thwarted by extensive compound decomposition at the same temperature, 715 K, for each sample filling. In the 1992 Project Report (Steele et al., 1996a) 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

$$\mathrm{BDE} = 64.7 \cdot R \cdot T$$

where BDE is bond dissociation energy in the same units as the gas constant R and T is the temperature of the onset of thermal decomposition. Applying that rule in this case leads to a bond dissociation energy of (380 ± 5) kJ·mol^{-1} in dimethyl isophthalate. Kerr (1966), revising the earlier values of Gray and Williams (1959), lists PhCO−OR′ bond dissociation energies of 377 kJ·mol^{-1} and 368 kJ·mol^{-1} for methyl and ethyl benzoates, respectively.

Dimethyl Carbonate. A critical temperature of (557 ± 1) K and a critical density of (358 ± 10) kg·m^{-3} were obtained from the fitting procedures used in this research for dimethyl carbonate. No other experimentally determined values for these properties were obtained in a search of the literature through January 1997.

Figure 4 compares values for the vapor pressure of dimethyl carbonate found in a literature search (Vogel, 1948; Wright, 1960; Cross et al., 1976; Jiang and Zhang, 1987) with values calculated using the Wagner equation and the parameters listed in Table 5.

Figure 5 compares values for the density of dimethyl carbonate found in a literature search (Kogerman and Kranig, 1927; Vogel, 1948; Thiebaut et al., 1976) with values calculated using eq 8 and the parameters listed in the footnotes to Table 4. [Only densities over a range of temperature were abstracted from the literature. Numerous single-point values (usually at 293 K) were also found in the search but excluded from consideration.] Agreement between the densities measured in this research and by both Kogerman and Kranig (1927) and Thiebaut et al. (1976) is excellent.

1,3,5-Triethylbenzene. A critical temperature of (679 ± 1) K and a critical density of (260 ± 10) kg·m^{-3} were obtained from the fitting procedures used in this research for 1,3,5-triethylbenzene. No experimentally determined values for these properties were found in a search of the literature. In fact, only one substantive reference was found to thermophysical property measurements on a sample of high purity. Gibbons et al. (1945) reported a

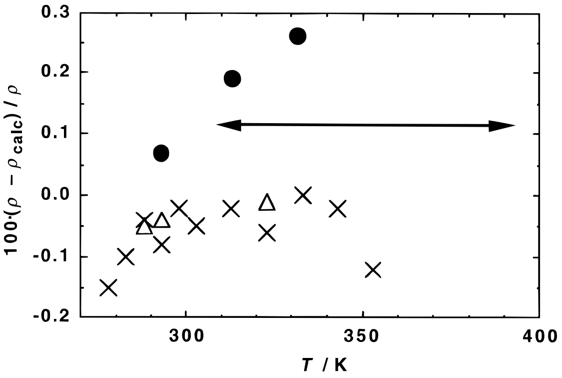

Figure 5. Comparison of literature values for the saturation liquid-phase density measurements for dimethyl carbonate with those obtained using eq 8 and the parameters listed in the footnotes to Table 4. The double-headed arrow represents the range of the measurements of this research and reported in Table 4. Key: (△) Kogerman and Kranig (1927); (●) Vogel (1948); (×) Thiebaut et al. (1976).

normal boiling point of 489.07 K (489.03 K on ITS-90) and a density of 862.1 kg·m^{-3} at 293 K for 1,3,5-triethylbenzene. Values obtained by interpolation and extrapolation of the measurements made in this research are 488.93 K and 860 kg·m^{-3} respectively.

Pentafluorophenol. A comprehensive range of thermochemical and thermophysical property measurements on pentafluorophenol was conducted at the National Physical Laboratory (NPL), Teddington, Middlesex, England, and published between 1968 and 1976 (Andon et al., 1968; Ambrose, 1968; Cox et al., 1969; Ambrose and Sprake, 1971; Hales and Townsend, 1974; Green and Harrison, 1976). Andon et al. (1968) described enthalpy and heat-capacity measurements on a sample of pentafluorophenol purified by zone refining. They list a purity of (99.97 ± 0.01) mol % obtained by fractional crystallization studies (Andon et al., 1968). That probably is an overestimation of the purity of the sample due to the purification technique used. Ambrose (1968) and later Ambrose and Sprake (1971) reported vapor-pressure measurements and estimated critical properties for pentafluorophenol. Cox et al. (1969) reported results of an enthalpy of formation study, which included details of enthalpy of sublimation measurements. Hales and Townsend (1974) measured densities along the saturation line in the temperature range 313 K to 490 K. Green and Harrison (1976) reported vibrational assignments and derived thermodynamic properties for a number of fluorocompounds including pentafluorophenol listing ideal-gas functions in the temperature range 273.15 K to 1500 K. Virtually simultaneous to the measurements of Andon et al. (1968), Paukov et al. (1969) also reported enthalpy, heat capacity, and phase transition measurements on pentafluorophenol in the temperature range 12.5 K to 328 K.

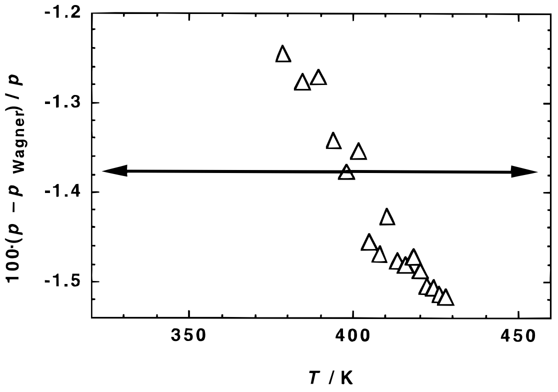

Figure 6. Comparison of the vapor pressures for pentafluorophenol reported by Ambrose (1968) and Ambrose and Sprake (1971) with values obtained using the Wagner equation and the parameters listed in Table 5. The double-headed arrow represents the range of the measurements of this research and reported in Table 1.

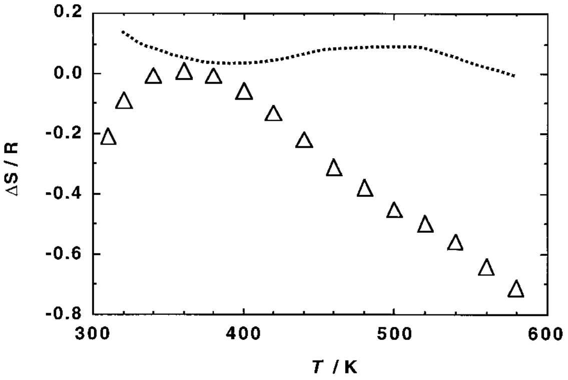

Figure 7. Comparison of the spectroscopic ideal-gas entropies for pentafluorophenol determined using the vibrational assignment of Green and Harrison (1976) with values derived from the calorimetric measurements. The dashed line represents the difference derived using the vapor pressures determined in this research. (△) Derived using NPL vapor pressures of Ambrose (1968) and Ambrose and Sprake (1971).

When the results reported in the literature for pentafluorophenol were reviewed, inconsistencies were evident. On attempting to fit the NPL vapor-pressure measurements using the Wagner equation and their listed critical properties, large deviations between the observed and calculated pressures were obtained. (Deviations fluctuated widely and were much larger than those obtained normally in such fits of NPL results.) In addition, as shown in Figure 7, the deviations between the ideal-gas entropy for pentafluorophenol derived from the calorimetric measurements reported by the NPL Group and the Green and Harrison (1976) reported functions were large and temperature dependent. This was particularly true if the heat-capacity measurements made at NIPER (Table 2 extending the temperature range of the measurements from 394 K to approximately 580 K) were used in the calculations. Therefore, the full range of thermophysical property measurements (vapor pressure, density, and high-temperature heat capacity) were determined at NIPER using a high-purity sample (>99.98 mol % by GLC).

Figure 6 compares the vapor pressures reported by Ambrose (1968) and Ambrose and Sprake (1971) with values obtained using the Wagner equation and the parameters listed in Table 5. The differences are large and can only be explained by the presence of an impurity.

In agreement with the observations of Ambrose and Sprake (1971), sample decomposition at approximately 600 K prevented any reliable experimentally determined measurement of the critical temperature of pentafluorophenol. The fitting procedures outlined above gave $T_c = (605 \pm 5)$ K, $p_c = (3800 \pm 300)$ kPa, and $\rho_c = (533 \pm 25)$ kg·m^{-3}. Ambrose and Sprake (1971) list estimates of $T_c = (609 \pm 5)$ K and $p_c = (4000 \pm 100)$ kPa.

Hales and Townsend (1974) measured liquid-phase densities for pentafluorophenol in the temperature range 313.15 K to 490 K as part of a series of measurements on eight fluorinated aromatic compounds. Differences between their measurements and those reported in Table 4 range from the NIPER values being 1% higher at 313 K to coincidence in density values at 448 K. It was noted by Hales and Townsend that "the pentafluorophenol sample became discolored and there was a reaction with the phosphor-bronze parts of the sample cell." No decomposi-

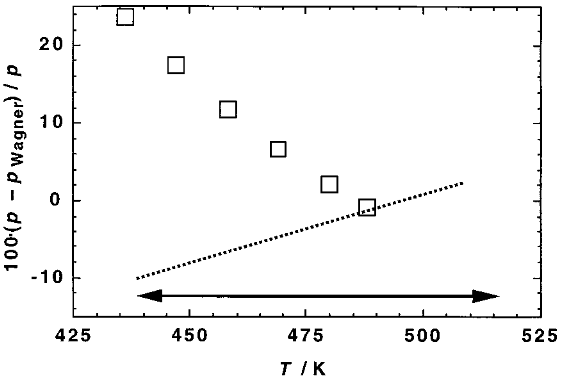

Figure 8. Comparison of literature vapor pressures for 4-*tert*-butylcatechol with values obtained using the Wagner equation and the parameters listed in Table 5. The double-headed arrow represents the range of the measurements of this research and reported in Table 1. The dashed line represents deviations of the DIPPR Project 801 correlation (Daubert and Danner, 1993). (□) Smith and Srivastava quoted reference (see text).

tion or reaction of the pentafluorophenol sample was evidenced during sample removal after the measurements reported in Table 4.

Figure 7 shows the deviations between the spectroscopic ideal-gas entropies for pentafluorophenol determined using the vibrational assignment of Green and Harrison (1976) and values derived from the calorimetric measurements. Using the NPL vapor pressures to derive enthalpies of vaporization, the deviation were significant and temperature dependent above 360 K. In contrast, using the results measured and derived in the NIPER research, the agreement between the spectroscopic and calorimetrically derived entropies is excellent between 300 K and 580 K and shows no significant temperature dependence.

4-tert-Butylcatechol. A critical temperature of (775 ± 5) K, a critical pressure of (3700 ± 300) kPa, and a critical density of (297 ± 15) kg·m^{-3} were obtained from the fitting procedures used in this research for 4-*tert*-butylcatechol. No experimentally determined values for these properties were obtained in a search of the literature. In fact, as in the case of 1,3,5-triethylbenzene, the literature search was most unproductive. Only one substantive reference was found to vapor-pressure measurements on 4-*tert*-butylcatechol. Smith and Srivastava (1986) reported the existence of a paper containing 20 vapor-pressure measurements in the temperature range 393 K to 489 K. However, the reference number, 7785, referred to in their table [Smith and Srivastava (1986), pp 722−723] is not listed in the bibliography for that volume. No such reference was found in the literature search conducted within this project; therefore, it was not possible to obtain the original data values.

Figure 8 compares values for the vapor pressure of 4-*tert*-butylcatechol listed by Smith and Srivastava and values derived applying the DIPPR Project 801 correlation (Daubert and Danner, 1993) with values calculated using the Wagner vapor-pressure equation and the parameters listed in Table 5.

The purified sample of 4-*tert*-butylcatechol used in the thermophysical property measurements of this research remained liquid for several weeks after purification before becoming an opaque solid. The small measured enthalpy of fusion and the small difference between the heat capacities of the solid and liquid phases (see Table 2) indicate that the solid phase at ambient temperature is only partially crystalline or retains a high degree of the molecular mobility present in the liquid.

Ribeiro da Silva et al. (1984) measured enthalpy increments for conversion of the solid at 298.15 K to the vapor at 380 K for several catechols, including 4-*tert*-butylcatechol, as part of a study of enthalpies of combustion and formation in the condensed and ideal-gas states. The experimentally measured values were "adjusted" to 298.15 K using estimates for the necessary heat capacities of the gas. Ribeiro da Silva et al. (1984) report an enthalpy of sublimation at 298.15 K, $\Delta_{\mathrm{c}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$ = (99.3 ± 1.4) kJ·mol^{-1} for 4-*tert*-butylcatechol. The corresponding value obtained in this research (see Tables 2 and 7) is (100.8 ± 2.8) kJ·mol^{-1}. The agreement between the results of Ribeiro da Silva et al. (1984) and the NIPER research points to both groups obtaining 4-*tert*-butylcatechol in the same solid form.

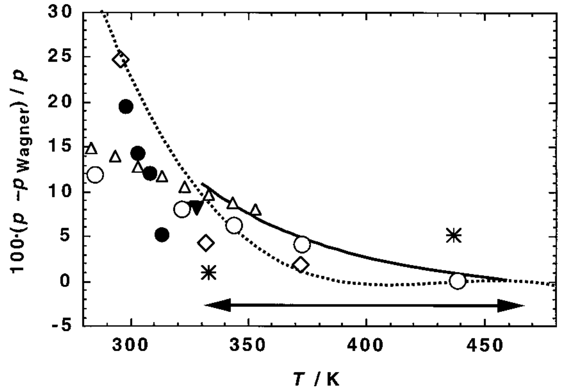

Figure 9. Comparison of literature vapor pressures for α-methylstyrene with values obtained using the Wagner equation and the parameters listed in Table 5. The doubled-headed arrow denotes the range of the vapor-pressure measurements obtained at NIPER. The solid line represents deviations of the DIPPR Project 801 correlation (Daubert and Danner, 1993). The dashed line represents deviations of the TRC listed vapor pressures (TRC, 1990). Key: (▼) Auwers et al. (1910, 1912); (○) Stull (1947); (*) Voronkov et al. (1949); (△) Laevskaya et al. (1979); (◇) Muthu et al. (1983); (●) Hamdouni et al. (1991).

α-Methylstyrene. Vapor pressures for α-methylstyrene have been reported by Auwers et al. (1910, 1912), Voronkov et al. (1949), Stull in his 1947 compilation of vapor pressures, Laevskaya et al. (1979), Muthu et al. (1983), and Hamdouni et al. (1991). In addition, TRC (1996) report vapor-pressure values over a wide range of temperature (269 K to 467 K). Figure 9 compares all the above-mentioned vapor-pressure measurements to values derived using the Wagner equation and the parameters listed in Table 5. Included in the figure is a curve representing the DIPPR 801 correlation equation over the same temperature range as that reported in Table 1.

A critical temperature of (645 ± 5) K, a critical pressure of (3550 ± 300) kPa, and a critical density of (288 ± 15) kg·m^{-3} were obtained from the fitting procedures used in this research for α-methylstyrene. No experimentally determined values for these properties were obtained in a search of the literature. Extensive polymerization prevents such measurements being accomplished with conventional equipment.

Figure 10 compares literature values for the density of α-methylstyrene (Tiffeneau, 1907; Hamdouni et al., 1991; TRC, 1996) with values calculated using eq 8 and the parameters listed in the footnotes to Table 4. Also shown is a solid line representing deviations from the DIPPR 801 density versus temperature equation.

Lebedev and Rabinovich (1971) reported heat capacities and thermodynamic functions for both α-methylstyrene and poly(α-methylstyrene) measured in an adiabatic calorimeter in the temperature region 60 K to 300 K. Extrapolation of the heat capacities, $C_{\mathrm{sat,m}}$, listed in Table 6 to the lower temperatures listed by Lebedev and Rabinovich (1971) shows good agreement.

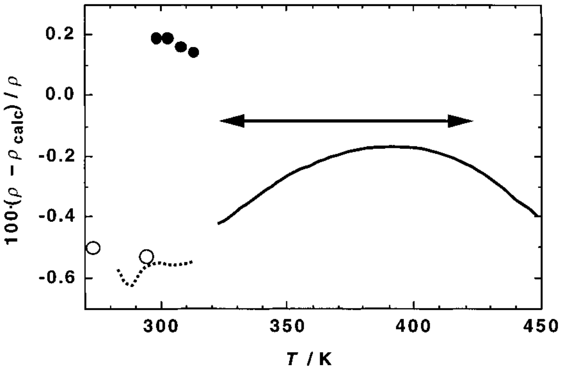

Figure 10. Comparison of literature values for the saturation liquid-phase density measurements for α-methylstyrene with those obtained using eq 8 and the parameters listed in the footnotes to Table 4. The doubled-headed arrow denotes the range of the liquid-phase density measurements obtained at NIPER. The solid line represents deviations of the DIPPR Project 801 correlation (Daubert and Danner, 1993). The dashed line represents deviations of the TRC listed densities (TRC, 1996). Key: (○) Tiffeneau (1907); (●) Hamdouni et al. (1991).

N,N′-Bis(2-hydroxyethyl)ethylenediamine. No thermophysical property measurements on *N,N′*-bis(2-hydroxyethyl)ethylenediamine were found in a search of the literature from 1930 through 1996.

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Literature Cited

Ambrose, D. Thermodynamic Properties of Fluorine Compounds. Part V. Vapour Pressures of Pentafluorobenzene, Chloropentafluorobenzene, 2,3,4,5,6-Pentafluorotoluene, and Pentafluorophenol. *J. Chem. Soc. A* **1968**, 1381−1383.

Ambrose, D.; Sprake, C. H. S. Thermodynamic Properties of Fluorine Compounds. Part X. Critical Properties and Vapour Pressures of Pentafluorobenzene, Chloropentafluorobenzene, 2,3,4,5,6-Pentafluorotoluene, and Pentafluorophenol. *J. Chem. Soc. A* **1971**, 1263−1266.

Ambrose, D.; Walton, J. Vapor Pressures up to Their Critical Temperatures of Normal Alkanes and 1-Alkanols. *Pure Appl. Chem.* **1989**, *61*, 1395−1403.

Ambrose, D.; Ewing, M. B.; Ghiassee, N. B.; Sanchez Ochoa, J. C. The Ebulliometric Method of Vapour-Pressure Measurement: Vapour Pressures of Benzene, Hexafluorobenzene, and Naphthalene. *J. Chem. Thermodyn.* **1990**, *22*, 589−605.

Andon, R. J. L.; Counsell, J. F.; Hales, J. L.; Lees, E. B.; Martin, J. F. Thermodynamic Properties of Fluorine Compounds. Part VII. Heat Capacity and Entropy of Pentafluorochlorobenzene and Pentafluorophenol. *J. Chem. Soc. A* **1968**, 2357−2361.

Auwers, von K.; Roth, W. A.; Eisenlohr, F. Thermochemical Investigations. III. Heats of Combustion of Terpenes and Styrenes. *Liebigs Ann. Chem.* **1910**, *373*, 267−290.

Auwers, von K.; Roth, W. A.; Eisenlohr, F. Thermochemical Investigations. IV. Heats of Combustion of Terpenes and Styrenes and Calculated Heat of Combustion. *Liebigs Ann. Chem.* **1912**, *385*, 102−116.

Bodnaryuk, F. N.; Korshavov, M. A.; Kislev, V. Ya.; Sumin, I. G. A New Method for Synthesizing Oligoester Acrylates. *Zh. Prikl. Khim. (Leningrad)* **1972**, *45*, 2500−2505.

Chirico, R. D.; Steele, W. V. Reconciliation Of Calorimetrically And Spectroscopically Derived Thermodynamic Properties at Pressures Greater Than 0.1 MPa for Benzene and Methylbenzene: The Importance of the Third Virial Coefficient. *Ind. Eng. Chem. Res.* **1994**, *33*, 157−167.

Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. Thermodynamic Properties of Biphenyl. *J. Chem. Thermodyn.* **1989a**, *21*, 1307−1331.

Chirico, R. D.; Nguyen, A.; Steele, W. V.; Strube, M. M.; Tsonopoulos, C. The Vapor Pressure of *n*-Alkanes Revisited. New Vapor Pressure Data on *n*-Decane, *n*-Eicosane and *n*-Octacosane. *J. Chem. Eng. Data* **1989b**, *34*, 149−156.

Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. The Thermodynamic Properties of Dibenzothiophene. *J. Chem. Thermodyn.* **1991**, *23*, 431−450.

Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K.; Steele, W. V. The Thermodynamic Properties of 4,5,9,10-Tetrahydropyrene and 1,2,3,6,7,8-Hexahydropyrene *J. Chem. Thermodyn.* **1993**, *25*, 729−761.

Cohen, E. R.; Taylor, B. N. The 1986 CODATA Recommended Values of the Fundamental Physical Constants. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1795−1803.

Colomina, M.; Laynez, J. L.; Perez-Ossono, R.; Turrion, C. Enthalpies of Combustion and Formation of Six Methyl Esters of Benzene Carboxylic Acids *J. Chem. Thermodyn.* **1972**, *4*, 499−506.

Cox, J. D.; Gundry, H. A.; Harrop, D.; Head, A. J. Thermodynamic Properties of Fluorine Compounds. 9. Enthalpies of Formation of some Compounds Containing the Pentafluorophenyl Group. *J. Chem. Thermodyn.* **1969**, *1*, 77−87.

Cross, J. D.; Hunter, R.; Stemson, V. R. The Thermal Decomposition of Simple Carbonate Esters. *Aust. J. Chem.* **1976**, *29*, 1477−1481.

Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; DIPPR Project 801; Hemisphere: New York, 1993.

Douslin, D. R.; McCullough, J. P. An Inclined-Piston Deadweight Pressure Gage. *Bur. Mines Rep. Invest.* **1963**, No. 6149, 11 pp.

Douslin, D. R.; Osborn, A. G. Pressure Measurements in the 0.01−30 mm Range with an Inclined-Piston Gauge. *J. Sci. Instrum.* **1965**, *42*, 369−373.

DuPont de Nemours. 4-Oxo-1,3-dioxanes. U.S. Patent 3,503,993, March 31, 1970; *Chem. Abstr.* **1970**, *73*, 14860Z.

Gibbons, L. C.; Thompson, J. F.; Reynolds, T. W.; Wright, J. I.; Chanan, H. H.; Lamberti, J. M.; Hipsher, H. F.; Karabinos, J. V. Purification and Physical Constants of Aromatic Hydrocarbons. *J. Am. Chem. Soc.* **1945**, *68*, 1130−1131.

Goldberg, R. N.; Weir, R. D. Conversion of Temperatures and Thermodynamic Properties to the Basis of the International Temperature Scale of 1990. *Pure Appl. Chem.* **1990**, *64*, 1545−1562.

Gray, P.; Williams, A. The Thermochemistry and Reactivity of Alkoxyl Radicals. *Chem. Rev.* **1959**, *59*, 239−328.

Green, J. H. S.; Harrison, D. J. Thermodynamic Properties of Fluorine Compounds. 19. Hexafluorobenzene, Pentafluorophenol, 1,3,5-Trichlorotrifluorobenzene, and Pentafluorobenzaldehyde: Vibrational Assignments and Chemical Thermodynamic Properties. *J. Chem. Thermodyn.* **1976**, *8*, 529−544.

Hales, J. L.; Townsend, R. Liquid Densities from 293 to 490 K of Nine Aromatic Hydrocarbons. *J. Chem. Thermodyn.* **1972**, *4*, 763−772.

Hales, J. L.; Townsend, R. Liquid Densities from 293 K to 490 K of Eight Fluorinated Aromatic Compounds. *J. Chem. Thermodyn.* **1974**, *6*, 111−116.

Hamdouni, A.; Leonard, J.; Bui, Van Tam Modeling Vapor Pressure Data of Ternary α-Methylstyrene-Toluene-Poly(α-methylstyrene) System. *Polym. J. (Tokyo)* **1991**, *23*, 219−226.

Hildebrand, J. H.; Scott, R. L. *Regular Solutions*; Prentice Hall: Englewood Cliffs, NJ, 1962.

IUPAC Commission on Atomic Weights and Isotopic Abundances. Atomic Weights of the Elements 1991. *J. Phys. Chem. Ref. Data* **1993**, *22*, 1571−1584.

Jiang, B.; Zhang, J. Determination and Correlation of Vapor Pressures of Dimethyl Carbonate and 2,3-Dichloropropene. *Tianjin Daxue Xuebao (Journal of Tianjin University)* **1987**, *1*, 54−62.

Kerr, J. A. Bond Dissociation Energies by Kinetic Methods. *Chem. Rev.* **1966**, *66*, 465−500.

Knipmeyer, S. E.; Archer, D. G.; Chirico, R. D.; Gammon, B. E.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Steele, W. V.; Strube, M. M. High-Temperature Enthalpy and Critical Property Measurements using a Differential Scanning Calorimeter. *Fluid Phase Equilib.* **1989**, *52*, 185−192.

Kogerman, P. N.; Kranig, J. Physical Constants of Some Alkyl Carbonates. *Acta Commentat. Univ. Tartu. (Dorpat.)* **1927**, *12* (7), 3−11.

Kucharenko, T. A.; Grigor'eva, E. A. *Neftekhymia* **1970**, *10*, 303−305.

Kraus, M.; Beranck, L.; Kochloefl, K.; Bazant, V. Vapor Pressure of Benzenecarboxylic Acids and their Derivatives. *Chem. Prum.* **1962**, *12*, 649−652.

Laevskaya, N. S.; Bagrov, I. V.; Dobroserdov, I. L.; Sokolkina, T. P. Liquid−Vapor Equilibrium of Systems Formed by Styrene with Benzene and a Series of its Derivatives. *Zh. Prikl. Khim (Leningrad)* **1979**, *52*, 687−689.

Lebedev, B. V.; Rabinovich, I. B. Heat Capacities and Thermodynamic Functions of α-Methyl-styrene and Poly(α-methylstyrene). *Tr. Khim. Khim. Tekhnol.* **1971**, *1*, 12−15.

Mangum, B. W.; Furukawa, G. T. Guidelines for Realizing the International Temperature Scale of 1990 (ITS-90). NIST Technical Note 1265; National Institute of Standards and Technology: Gaithersburg, MD, 1990.

Murogova, R. A.; Tudorosvakaya, G. L.; Laufer, V. V.; Kozlova, V. D.; Serafimov, L. A. Liquid–Vapor Equilibrium in Systems Formed by Esterification Products of Isophthalic Acid at a Pressure of 15 mm Mercury. *J. Appl. Chem. USSR* **1974**, *47*, 2079–2081.

Muthu, O.; Munjal, S.; Smith, B. D. Total Pressure Vapor–Liquid Equilibria Data for Binary Systems of Acetone with Isopropylbenzene and Isopropenylbenzene. *J. Chem. Eng. Data* **1983**, *28*, 192–196.

Orbey, H.; Vera, J. H. Correlation for the Third Virial Coefficient using T_c, p_c, and ω as Parameters. *AIChE J.* **1983**, *29*, 107–113.

Osborn A. G.; Douslin, D. R. Vapor Pressure Relations of 36 Sulfur Compounds Present in Petroleum. *J. Chem. Eng. Data* **1966**, *11*, 502–509.

Paukov, I. E.; Lavrent'eva, M. N.; Anisimov, M. P. Heat Capacity, Phase Transitions, Entropy, and Enthalpy of Pentafluorophenol at Low Temperatures. *Russ. J. Phys. Chem.* **1969**, *43*, 436–438.

Pitzer, K. S.; Curl, R. F., Jr. The Volumetric and Thermodynamic Properties of Fluids. III. Empirical Equation for the Second Virial Coefficient. *J. Am. Chem. Soc.* **1957**, *79*, 2369–2370.

Ribeiro da Silva, M. D. M. C.; Ribeiro da Silva, M. A. V.; Pilcher, G. Enthalpies of Combustion Of 1,2-Dihydroxybenzene and of Six Alkylsubstituted 1,2-Dihydroxybenzenes. *J. Chem. Thermodyn.* **1984**, *16*, 1149–1155.

Riedel, L. Liquid Density in the Saturated State. Extension of the Theorem of Corresponding States II. *Chem.-Ing.-Tech.* **1954**, *26*, 259–264.

Scott, D. W.; Finke, H. L.; Gross, M. E.; Guthrie, G. B.; Huffman, H. M. 2,3-Dithiabutane: Low Temperature Heat Capacity, Heat of Fusion, Heat of Vaporization, Vapor Pressure, Entropy, and Thermodynamic Functions *J. Am. Chem. Soc.* **1950**, *72*, 2424–2430.

Smith, B. D.; Srivastava, R. *Thermodynamic Data for Pure Compounds. Part B. Halogenated Hydrocarbons and Alcohols*; Physical Sciences Data 25; Elsevier: New York, 1986.

Steele, W. V. Fifty Years of Thermodynamics Research at Bartlesville. The Hugh M. Huffman Legacy. *J. Chem. Thermodyn.* **1995**, *27*, 135–162.

Steele, W. V. Unpublished results, 1996.

Steele, W. V.; Archer, D. G.; Chirico, R. D.; Collier, W. B.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Gammon, B. E. The Thermodynamic Properties of Quinoline and Isoquinoline. *J. Chem. Thermodyn.* **1988a**, *20*, 1233–1264.

Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Smith, N. K. High-Temperature Heat-Capacity Measurements and Critical Property Determinations using a Differential Scanning Calorimeter (Development of Methodology and Application to Pure Organic Compounds). NIPER-360; DOE Fossil Energy, Bartlesville Project Office: Bartlesville, OK, December 1988b. Available from NTIS Order No. DE89000709.

Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. The Thermodynamic Properties of 2-Aminobiphenyl. *J. Chem. Thermodyn.* **1991**, *23*, 957–977.

Steele, W. V.; Chirico, R. D.; Nguyen, A.; Knipmeyer, S. E. Vapor Pressures, High-Temperature Heat Capacities, Critical Properties, Derived Thermodynamic Functions, and Barriers to Methyl-Group Rotation, for the Six Dimethylpyridines. *J. Chem. Thermodyn.* **1995**, *27*, 311–334.

Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Vapor Pressure of Acetophenone, (±)-1,2-Butanediol, (±)-1,3-Butanediol, Diethylene Glycol Monopropyl Ether, 1,3-Dimethyladamantane, 2-Ethoxyethyl Acetate, Ethyl Octyl Sulfide, and Pentyl Acetate. *J. Chem. Eng. Data* **1996a**, *41*, 1255–1268.

Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K.; Tasker, I. R. Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Cyclohexene, Phthalan (2,5-Dihydrobenzo-3,4-furan), Isoxazole, Octylamine, Dioctylamine, Trioctylamine, Phenyl Isocyanate, and 1,4,5,6-Tetrahydropyrimidine. *J. Chem. Eng. Data* **1996b**, *41*, 1269–1284.

Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K. Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Butyl Vinyl Ether, 1,2-Dimethoxyethane, Methyl Glycolate, Bicyclo[2.2.1]hept-2-ene, 5-Vinylbicyclo[2.2.1]-hept-2-ene, *trans*-Azobenzene, Butyl Acrylate, Di-*tert*-butyl Ether, and Hexane-1,6-diol. *J. Chem. Eng. Data* **1996c**, *41*, 1285–1302.

Stull, D. R. Vapor Pressures of Pure Substances. Organic Compounds. *Ind. Eng. Chem.* **1947**, *39*, 518–550; **1947**, *39*, 1684.

Swietoslawski, W. *Ebulliometric Measurements*; Reinhold: New York, 1945.

Thiebaut, J.-M.; Rivail, J.-L.; Greffe, J.-L. Dielectric Studies of Non Electrolyte Solutions. Part 3 Conformational Equilibria in 1,2-Dichloroethane and Dimethyl Carbonate. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 2024–2034.

Tiffeneau, M. Benzene Hydrocarbons with a Pseudo-Allyl Side Chain: Methovinyl Benzene and its Homologues. *Ann. Chim. Phys. (Paris)* **1907**, *10*, 145–198.

TRC Thermochemical Tables-Hydrocarbons. (Formerly API Research Project 44, then TRC Hydrocarbon Project. Selected Values of Properties of Hydrocarbons and Related Compounds, Category A. Tables of Physical and Thermodynamic Properties.) Thermodynamics Research Center, Texas A&M University: College Station, TX, Extant 1996.

Vogel, A. I. XXIII Miscellaneous Compounds. Investigations of the So-called Coordinate or Dative Link in Esters of Oxy Acids and in Nitro Paraffins by Molecular Refractivity Determinations. Atomic, Structural, and Group Parachors and Refractivities. *J. Chem. Soc.* **1948**, 1833–1855.

Voronkov, M. G.; Broun, A. S.; Karpenko, G. P.; Gol'shtein, B. L. Reactions of Sulfur with Unsaturated Compounds. III. Synthesis of 2-Phenylthiophene. *Zh. Obshch. Khim.* **1949**, *19*, 1356–1364.

Wagner, W. New Vapor Pressure Measurements for Argon and Nitrogen and a New Method for Establishing Rational Vapor Pressure Equations. *Cryogenics* **1973**, *13*, 470–482.

Wegscheider, R.; Perdanner, H. I.; Auspitzer, O. Esterification of Unsymmetric Di- and Polybasic Acids. XXXIII. Trimellitic Acid. *Monatsh. Chem.* **1911**, *31*, 1253–1301.

Wright, F. J. Latent Heat of Vaporization and Composition. *Recl. Trav. Chim. Pays-Bas* **1960**, *79*, 784–789.

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