Vapor Pressure, Heat Capacity, and Density along the Saturation Line: Measurements for Benzenamine, Butylbenzene, *sec*-Butylbenzene, *tert*-Butylbenzene, 2,2-Dimethylbutanoic Acid, Tridecafluoroheptanoic Acid, 2-Butyl-2-ethyl-1,3-propanediol, 2,2,4-Trimethyl-1,3-pentanediol, and 1-Chloro-2-propanol

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This paper reports measurements made within DIPPR[2] Project 821 for the 1995 Project Year. Vapor pressures were measured to a pressure limit of 270 kPa or lower decomposition point using a twin ebulliometric apparatus for the nine compounds listed in the title. Liquid-phase densities along the saturation line were measured for each compound over a range of temperatures (ambient to a maximum of 523 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. 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 310 K, solubility parameters, and heat capacities along the saturation line. Vapor-pressure representations were derived for each compound. 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 except 1-chloro-2-propanol. The compounds studied were benzenamine, butylbenzene, *sec*-butylbenzene, *tert*-butylbenzene, 2,2-dimethylbutanoic acid, tridecafluoroheptanoic acid, 2-butyl-2-ethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, and 1-chloro-2-propanol.

Introduction

DIPPR's goal is to develop, organize, maintain, and make available reliable physical, thermodynamic, and transport property data for industrially important chemical compounds. Work is in progress compiling data on >1600 chemicals important to industry. Where no data exist, estimation is attempted. These estimations require a strong base of accurate and precise data on basic molecular structures. The main goal in this research, Project 821, is to obtain accurate and precise vapor-pressure measurements on key organic chemicals over as wide a temperature range as possible. A second goal is to derive accurate means of representing the vapor pressures mathematically and correlating them with other thermophysical properties.

The objectives of this research program can be summarized as follows: to obtain, analyze, and purify (to a minimum purity level of 99.9 mole %) 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 523 K if possible) for each compound; and to fit the measured vapor pressures to a vapor-pressure equation. The Wagner[1] equation in the formulation given by Ambrose and Walton,[2]

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

where $T_r = T/T_c$ and $Y = (1 - T_r)$, or the Antoine equation,

$$\lg(p/p_{ref}) = A + B/[(T/K) + C] \qquad (2)$$

with $p_{ref} = 1$ kPa, was used. Fitting procedures were used to determine heat capacities along the saturation line and derive the critical pressure; where possible 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.

For over 50 years the Bartlesville (NIPER) laboratory was at the forefront of technical development in the

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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 have been published.[3−8] 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 (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 can be readily detected at levels as low as 0.1%.

A goal of this project is to determine the vapor pressure up to the critical point or lower decomposition point. 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 ref 9) would enable measurements to the critical point, provided the presence of the metal surface did not catalyze sample decomposition. The development of a metal twin-ebulliometric vapor-pressure apparatus at ORNL to make experimental measurements in the high-pressure region is under consideration. However, because of the period of time required to make such measurements (0.25 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 together with accurate vapor pressures in the region below 270 kPa, it has been shown[10−12] 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 was the extension of the temperature limits of the in-house apparatus. In the area of heat-capacity measurements, this was fulfilled by the development of a DSC technique (applicable to 950 K[13]) to measure heat capacities to within 20 K of the critical point.[10,11] Combination of measured two-phase (liquid + vapor) heat capacities (obtained for a minimum of three cell fillings) and vapor-pressure data (measured within the inclined-piston and ebulliometric regions) has enabled estimation of the critical pressure for many substances. The fitting procedures used have been described.[10,11,13] In addition, where sample decomposition does not occur or is sufficiently slow, 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 also requires an accurate knowledge of the liquid-phase density. Hence, a vibrating-tube densitometer capable of measurements from ambient to 523 K (the temperature limit of the bath used in the measurements) was constructed at NIPER. Results obtained from the densitometer measurements are included in the fitting procedures used to derive the thermophysical properties reported in this paper.

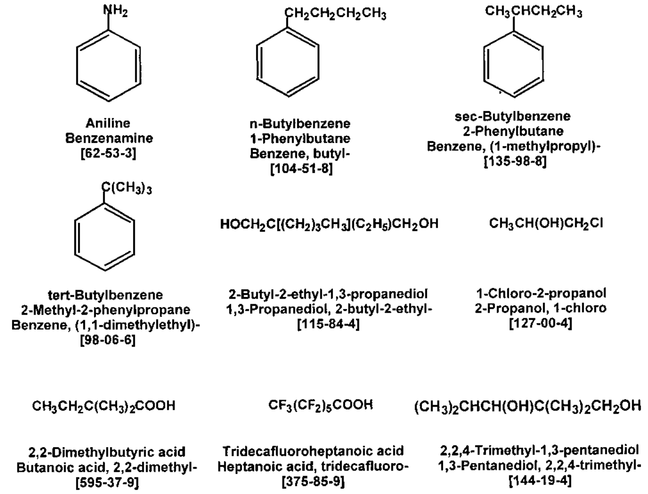

Figure 1. Structural formulas, common names, Chemical Abstracts Service names (provided by the authors), and Chemical Abstracts Service Registry Numbers (CAS No.) (provided by the authors) for the compounds studied in this research.

Figure 1 lists the structural formulas, names, and Chemical Abstracts Service registry numbers (CAS No.) (supplied by the authors) for each of the compounds studied in the 1995 project year for Project 821. The bottom name listed below each structure denotes that used presently by Chemical Abstracts.

Experimental Section

The apparatus and procedures used in obtaining the experimental data have been previously described in the literature and in various DOE reports. Therefore, in this paper no details are given and the reader is referred to refs 14−16 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 used in the thermophysical property measurements. All compounds except 1-chloro-2-propanol were purchased from Aldrich Chemical Co. Gas−liquid chromatographic (GLC) analyses on the purchased samples gave an average purity of 98 mol %, in agreement with Aldrich specifications. The purchased compounds were purified 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. The sample of 1-chloro-2-propanol used in the measurements reported in this research was obtained from Dow Chemical Company, Texas Operations, Freeport, TX. Since the initial GLC analysis of the sample showed a purity > 99.95 mol %, no further purification was attempted.

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 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

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
A. Wagner-Equation Fit[b]											
Benzenamine											
decane	349.967	1.9995	0.0000	0.0001	0.028	water	430.262	47.363	0.001	0.002	0.004
decane	364.273	3.9974	0.0002	0.0003	0.015	water	436.946	57.812	0.001	0.003	0.004
decane	370.659	5.3303	0.0000	0.0003	0.014	water	443.662	70.106	−0.002	0.003	0.004
decane	380.135	7.9913	0.0002	0.0005	0.010	water	450.420	84.516	0.000	0.004	0.005
decane	387.262	10.6616	−0.0001	0.0006	0.007	water	457.219	101.307	0.000	0.005	0.006
decane	392.957	13.299	0.000	0.001	0.006	water	464.055	120.76	0.00	0.01	0.008
decane	398.984	16.660	−0.001	0.001	0.005	water	470.937	143.22	0.00	0.01	0.009
decane	403.934	19.924	0.000	0.001	0.005	water	477.858	169.00	0.00	0.01	0.012
decane	410.468	25.021	0.000	0.001	0.004	water	484.819	198.46	−0.01	0.01	0.013
water	410.481[c]	25.033	0.001	0.001	0.004	water	491.823	232.01	−0.01	0.01	0.018
water	417.012	31.157	0.000	0.002	0.004	water	498.846	269.94	0.01	0.01	0.025
water	423.615	38.544	0.000	0.002	0.004						
Butylbenzene											
decane	343.359	1.9971	0.0001	0.0001	0.032	water	427.754	47.388	−0.002	0.002	0.001
decane	358.262	3.9918	−0.0002	0.0003	0.017	water	434.837	57.826	0.000	0.003	0.002
decane	364.913	5.3190	−0.0001	0.0003	0.012	water	441.972	70.118	−0.001	0.003	0.003
decane	374.873	7.9884	0.0001	0.0005	0.007	water	449.160	84.517	−0.001	0.004	0.002
decane	382.365	10.6646	−0.0001	0.0006	0.005	water	456.418	101.336	−0.001	0.004	0.001
decane	388.426	13.340	0.000	0.001	0.004	water	463.720	120.81	0.00	0.01	0.001
decane	394.691	16.667	0.001	0.001	0.003	water	471.064	143.25	0.00	0.01	0.001
decane	399.906	19.931	0.001	0.001	0.002	water	478.460	169.01	0.00	0.01	0.000
decane	406.785	25.019	0.000	0.001	0.002	water	485.916	198.48	0.00	0.01	0.000
water	406.788[c]	25.022	0.001	0.001	0.001	water	493.422	232.02	0.00	0.01	0.000
water	413.742	31.196	0.000	0.002	0.001	water	500.970	270.02	0.00	0.01	0.002
water	420.712	38.570	0.000	0.002	0.001						
sec-Butylbenzene											
decane	334.673	2.0006	0.0001	0.0001	0.021	water	418.033	47.366	0.000	0.002	0.000
decane	349.434	4.0087	−0.0001	0.0003	0.010	water	425.045	57.792	−0.001	0.003	0.000
decane	355.963	5.3319	−0.0002	0.0003	0.007	water	432.134	70.119	0.000	0.003	0.000
decane	365.767	7.9965	0.0004	0.0005	0.004	water	439.260	84.526	0.000	0.004	0.000
decane	373.147	10.6650	−0.0003	0.0006	0.003	water	446.439	101.308	−0.001	0.004	−0.001
decane	379.143	13.343	0.000	0.001	0.002	water	453.685	120.80	0.00	0.01	−0.001
decane	385.317	16.658	0.000	0.001	0.002	water	460.978	143.26	0.00	0.01	0.000
decane	390.481	19.925	0.000	0.001	0.001	water	468.321	169.04	0.00	0.01	−0.001
decane	397.293	25.017	0.000	0.001	0.000	water	475.711	198.48	0.00	0.01	−0.001
water	397.297[c]	25.022	0.001	0.001	0.000	water	483.158	232.01	0.00	0.01	−0.001
water	404.156	31.173	0.000	0.002	0.000	water	490.656	270.01	0.00	0.01	−0.001
water	411.080	38.573	0.001	0.002	0.000						
tert-Butylbenzene											
decane	331.641	2.0000	−0.0001	0.0001	0.031	water	414.111	47.373	−0.001	0.002	0.000
decane	346.094	3.9851	−0.0002	0.0003	0.010	water	421.051	57.793	0.002	0.003	0.001
decane	352.699	5.3378	0.0005	0.0003	0.010	water	428.086	70.135	−0.001	0.003	−0.002
decane	362.386	8.0013	−0.0001	0.0005	0.009	water	435.141	84.532	0.004	0.004	−0.001
decane	369.654	10.6598	0.0006	0.0006	0.005	water	442.255	101.310	0.005	0.004	−0.001
decane	375.553	13.321	0.001	0.001	0.003	water	449.430	120.77	0.01	0.01	0.000
decane	381.692	16.647	0.000	0.001	0.004	water	456.676	143.27	0.00	0.01	−0.002
decane	386.829	19.929	−0.001	0.001	0.003	water	463.956	169.03	0.00	0.01	−0.002
decane	393.580	25.029	−0.001	0.001	0.001	water	471.296	198.49	−0.01	0.01	−0.003
water	393.571[c]	25.019	−0.003	0.001	0.000	water	478.687	232.01	0.00	0.01	−0.003
water	400.370	31.179	−0.004	0.002	0.000	water	486.135	270.02	0.00	0.01	−0.004
water	407.219	38.573	−0.001	0.002	0.000						
2,2-Dimethylbutanoic Acid											
decane	363.835	1.9924	0.0005	0.0001	0.051	water	437.055	47.366	0.003	0.003	0.008
decane	377.204	3.9998	−0.0003	0.0003	0.034	water	443.015	57.814	0.003	0.003	0.008
decane	383.053	5.3219	−0.0014	0.0003	0.025	water	448.993	70.117	0.001	0.004	0.009
decane	391.825	8.0076	−0.0004	0.0005	0.023	water	454.987	84.515	0.001	0.004	0.008
decane	398.307	10.6700	−0.0001	0.0006	0.020	water	461.013	101.309	−0.003	0.005	0.008
decane	403.525	13.329	0.000	0.001	0.017	water	467.061	120.77	−0.01	0.01	0.006
decane	408.953	16.671	0.000	0.001	0.014	water	473.152	143.27	−0.02	0.01	0.008
decane	413.412	19.922	0.002	0.001	0.013	water	479.241	168.98	−0.03	0.01	0.013
decane	419.293	25.007	0.001	0.001	0.011	water	485.375	198.45	−0.02	0.01	0.017
water	419.321[c]	25.034	0.002	0.002	0.010	water	491.534	231.98	0.00	0.01	0.025
water	425.205	31.173	0.004	0.002	0.009	water	497.720	269.97	0.06	0.01	0.036
water	431.120	38.558	0.004	0.002	0.009						
Tridecafluoroheptanoic Acid											
decane	359.074	1.9980	0.0001	0.0002	0.040	water	427.369	47.369	0.001	0.003	0.017
decane	371.394	3.9919	0.0000	0.0003	0.023	water	432.985	57.802	−0.004	0.003	0.013
decane	376.901	5.3323	−0.0005	0.0004	0.019	water	438.648	70.136	−0.003	0.004	0.015
decane	385.002	7.9982	−0.0005	0.0005	0.013	water	444.318	84.519	−0.006	0.004	0.014
decane	391.081	10.6784	−0.0008	0.0006	0.013	water	450.030	101.304	−0.007	0.005	0.014
decane	395.927	13.328	0.001	0.001	0.013	water	455.777	120.77	0.00	0.01	0.014
decane	400.977	16.656	0.001	0.001	0.014	water	461.560	143.22	0.00	0.01	0.014
decane	405.187	19.937	0.001	0.001	0.014	water	467.373	169.00	0.02	0.01	0.016
decane	410.691	25.025	0.002	0.001	0.014	water	473.223	198.45	0.01	0.01	0.016
water	410.705[c]	25.039	0.002	0.002	0.013	water	479.111	232.01	0.01	0.01	0.021
water	416.226	31.179	0.000	0.002	0.013	water	485.030	270.00	−0.02	0.01	0.022
water	421.789	38.570	0.000	0.002	0.014						

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
B. Antoine-Equation Fit[d]											
2-Butyl-2-ethyl-1,3-propanediol											
decane	424.536	2.0044	0.0003	0.0001	0.073	water	487.749	25.027	−0.002	0.001	0.023
decane	439.340	3.9958	0.0000	0.0003	0.061	water	494.634	31.164	0.002	0.002	0.023
decane	445.970	5.3220	−0.0004	0.0003	0.057	water	501.594	38.562	0.009	0.002	0.026
decane	455.909	7.9936	0.0013	0.0005	0.050	water	508.602	47.377	0.006	0.002	0.029
decane	463.358	10.6566	−0.0012	0.0006	0.039	water	515.652	57.813	−0.003	0.003	0.033
decane	469.421	13.337	−0.002	0.001	0.035	water	522.761	70.132	−0.013	0.003	0.046
decane	475.697	16.678	−0.001	0.001	0.030	water	529.903[f]	84.495	−0.067	0.004	0.059
decane	480.875	19.931	0.003	0.001	0.028	water	537.094[f]	101.284	−0.082	0.006	0.073
decane	487.713[e]	25.015	0.015	0.001	0.027						
1-Chloro-2-propanol											
decane	308.758	2.0004	0.0149	0.0002	0.077	water	359.882[g]	25.030	0.112	0.002	0.066
decane	320.981	3.9935	−0.0076	0.0003	0.068	water	365.489	31.185	0.037	0.002	0.051
decane	326.457	5.3340	−0.0226	0.0004	0.066	water	371.029	38.555	0.045	0.002	0.055
decane	334.439	7.9821	−0.0344	0.0005	0.062	water	376.582	47.354	0.090	0.003	0.060
decane	340.451	10.6634	−0.0247	0.0006	0.061	water	382.215	57.802	0.061	0.003	0.061
decane	345.282	13.333	−0.010	0.001	0.060	water	387.830	70.095	0.105	0.004	0.070
decane	350.276	16.656	0.011	0.001	0.067	water	393.520	84.495	0.026	0.004	0.076
decane	354.438	19.926	0.034	0.001	0.063	water	399.256	101.314	−0.103	0.005	0.074
decane	359.933	25.019	0.049	0.001	0.061	water	405.024[h]	120.75	−0.35	0.01	0.084
2,2,4-Trimethyl-1,3-pentanediol											
decane	395.954	2.0002	0.0052	0.0001	0.036	water	456.045[g]	25.028	0.025	0.001	0.003
decane	410.132	3.9974	−0.0052	0.0003	0.024	water	462.607	31.182	0.031	0.002	0.003
decane	416.450	5.3285	−0.0081	0.0003	0.017	water	469.220	38.567	0.030	0.002	0.003
decane	425.845	7.9887	−0.0091	0.0005	0.010	water	475.901	47.393	0.013	0.002	0.004
decane	432.906	10.6526	−0.0065	0.0006	0.007	water	482.611	57.820	−0.020	0.003	0.005
decane	438.680	13.346	−0.001	0.001	0.005	water	489.387	70.111	−0.096	0.003	0.007
decane	444.590	16.664	0.006	0.001	0.004	water	496.221[h]	84.524	−0.207	0.005	0.010
decane	449.544	19.941	0.012	0.001	0.003	water	503.102[h]	101.310	−0.361	0.006	0.019
decane	456.013	24.999	0.023	0.001	0.002						

[a] Water or decane refers to which material was used as the standard 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; σ is the propagated error calculated using eq 4; ΔT is the difference between the boiling and condensation temperatures ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the sample. [b] 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 ($\Delta p = p - p_{\mathrm{Wagner}}$). [c] Values at this temperature were not included in the fit of the Wagner equation. The measurement was an overlap point between the use of decane and water as the pressure measurement standards. [d] $\Delta p = p - p_{\mathrm{Antoine}}$ is the difference of the value of the pressure calculated using eq 2 (see text) from the observed value of pressure. [e] Value appears to be in error. It would appear that the temperature of either the compound or the standard was misread by the computer control program. [f] Values at this temperature were not included in the fit of the Antoine equation because sample decomposition was indicated by the increase in the ΔT values. [g] Values at this temperature were not included in the fit of the Antoine equation. The measurement was an overlap point between the use of decane and water as pressure measurement standards. [h] Values at this temperature were not included in the fit of the Antoine equation.

kPa pressure. GLC analysis of the decane sample failed to show any impurity peaks.

Physical Constants. Molar values are reported in terms of the 1991 relative atomic masses[17] and the gas constant, $R = 8.314\,51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, adopted by CODATA.[18] The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Institute of Standards and Technology (NIST). All temperatures are reported in terms of ITS-90.[19,20] Measurements of mass, time, electric resistance, and potential difference were performed in terms of standards traceable to calibrations at NIST.

Vapor Pressure Apparatus and Procedures. The essential features of the ebulliometric equipment and procedures for vapor-pressure measurements are described in the literature.[3−5] The ebulliometers were used to reflux the substance under study with a standard of known vapor pressure under a common helium atmosphere. In the pressure region 25 kPa to 270 kPa, water was used as the standard, and the pressures were derived using the internationally accepted equation of state for ordinary water revised to ITS-90.[21] In the pressure region 2 kPa to 25 kPa, decane was used as the standard. Pressures were calculated on ITS-90 for those measurements using the equation

$$\ln(p/\mathrm{kPa}) = 7.73165 + (1/T_{\mathrm{r}})\{-9.98917(1 - T_{\mathrm{r}}) + 5.28411(1 - T_{\mathrm{r}})^{1.5} - 6.51326(1 - T_{\mathrm{r}})^{2.5} - 2.68400(1 - T_{\mathrm{r}})^{5}\} \quad (3)$$

where $T_{\mathrm{r}} = T/(617.650\ \mathrm{K})$ and T denotes the condensation temperature for decane.

The precision in the temperature measurements for the ebulliometric vapor-pressure studies was 0.001 K. Uncertainties in the pressures are adequately described by

$$\sigma(p) = (0.001)\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_{\mathrm{samp}}/\mathrm{d}T)^2\}^{1/2} \quad (4)$$

where p_{ref} is the vapor pressure of the reference substance and p_{samp} is the vapor pressure of the sample under study.

Densitometry. Densities, ρ, at saturation pressure for the liquid phase for a range of temperatures were obtained in this research with a vibrating-tube densitometer. The densitometer design is essentially that used successfully by Dr. J. M. Simonson and his colleagues at Oak Ridge National Laboratory for the study of aqueous salt mixtures at high temperatures and pressures.[22] The instrument and its operation have been described.[23] Test measurements of the density of benzene between $T = 310$ K and $T = 523$ K have been reported.[24] Results agreed with published values[25] within $(1 \times 10^{-3})\rho$. The precision of the measurements was approximately $(5 \times 10^{-4})\rho$.

Differential Scanning Calorimetry. The technique and methodology used in the differential scanning calorimetry (DSC) measurements have been described.[8,11−13,24,26] The major difference between our measurement technique and that used by Mraw and Naas[27] is the substitution of specially designed cells[8] for the aluminum "volatile sample cells." These cells, designed and manufactured at NIPER, are made of 17-4 PH stainless steel and can withstand both high pressures (to 7.6 MPa) and high temperatures (to >950 K). The theoretical background for the determination of heat capacities at vapor-saturation pressure, $C_{\mathrm{sat,m}}$, from $C_{x,\mathrm{m}}^{\mathrm{II}}$ values obtained with DSC has been described.[8,11−13,24,26] The review by Steele[13] is detailed and will be referenced throughout this paper.

Results

Vapor Pressures. Measured vapor pressures for each of the compounds studied are listed in Table 1. The vapor pressures, the condensation temperatures, and the difference between the condensation and boiling temperatures ($\Delta T = T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the samples are reported. The small and constant (over a wide pressure range) differences between the boiling and condensation temperatures in the ebulliometric measurements indicated correct operation of the equipment and the high purity of the samples. In Table 1B 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 2-butyl-2-ethyl-1,3-propanediol above 523 K, for 1-chloro-2-propanol above 400 K, and for 2,2,4-trimethyl-1,3-pentanediol above 496 K. Although the Wagner equation fit (see Table 1A) for benzenamine does not show it and fast-scan DSC critical-region results were obtained (see Table 3), the increase in ΔT above the normal boiling point indicates that slow decomposition was occurring.

Differential Scanning Calorimetry. Table 2 lists the two-phase heat capacities $C_{x,\mathrm{m}}^{\mathrm{II}}$ determined by DSC for each of the compounds. 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 heats. For each compound the upper temperature bound of the measurements was set by the critical region or earlier sample decomposition.

For 2,2-dimethylbutanoic acid, tridecafluoroheptanoic acid, 2-butyl-2-ethyl-1,3-propanediol, 1-chloro-2-propanol, and 2,2,4-trimethyl-1,3-pentanediol, extensive sample decomposition precluded attainment of heat-capacity measurements above the highest listed temperatures. For benzenamine, and the three butylbenzenes, measurements in the critical region were possible. For 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, V_x, calculated with eq 5, and the measured temperatures at which conversion to a single phase was observed. In this research, the thermal expansion of the cells was expressed as

$$V_x(T)/V_x(298.15\ \mathrm{K}) = 1 + ay + by^2 \qquad (5)$$

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

Critical temperatures and critical densities were derived graphically for benzenamine, butylbenzene, *sec*-butylbenzene, and *tert*-butylbenzene, as seen in Figure 2. Results of measurements on benzene and toluene performed as "proof-of-concept measurements" for these procedures have been reported.[24] The rapid heating method was used previously for critical temperature and critical density determinations for 2-aminobiphenyl,[28] dibenzothiophene,[29] carbazole, and benzofuran.[13]

Tridecafluoroheptanoic acid, 2-butyl-2-ethyl-1,3-propanediol, and 2,2,4-trimethyl-1,3-pentanediol are solids at ambient temperature. By judicious choice of starting temperature, the melting endotherms during the DSC enthalpy measurements for each compound occurred in the center of a heating cycle. The measured enthalpies during those 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. A derived enthalpy of fusion at the melting point is reported for tridecafluoroheptanoic acid, 2-butyl-2-ethyl-1,3-propanediol, and 2,2,4-trimethyl-1,3-pentanediol in Table 2.

Densitometry. Measured densities for each of the compounds in the liquid phase along the saturation line are listed in Table 4. The temperatures are precise to 0.005 K. As shown in ref 24, the expected accuracy of the densities is 0.1 kg·m^{-3}.

Fitting Procedures. For the compounds benzenamine, the three butylbenzenes, 2,2-dimethylbutanoic acid, and tridecafluoroheptanoic acid (i.e., compounds with vapor-pressure measurements between 2 kPa and 270 kPa), the same general fitting procedures were used. The number of fitting parameters differed depending on whether a critical temperature could be determined experimentally. For both 2,2-dimethylbutanoic acid and tridecafluoroheptanoic acid, extensive high-temperature sample decomposition precluded critical temperature measurements and, therefore, both T_{c} and p_{c} were included as variables. For benzenamine and the butylbenzenes, critical temperatures were determined from the DSC measurements and, hence, only the critical pressure p_{c} was included in the variables. 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 $C_{x,\mathrm{m}}^{\mathrm{II}}$ given in Table 2. A summary of the procedure follows.

The Wagner equation[1] (eq 1) was fitted to the measured vapor pressures (Table 1A). As noted above, the critical pressure p_{c} (and, for 2,2-dimethylbutanoic acid and tridecafluoroheptanoic acid, the critical temperature T_{c}) was (were) included in the variables. The vapor-pressure fitting procedure including the minimization equation and the relative weightings has been published.[13]

For fitting the two-phase heat capacities obtained in a cell of volume V_x, the experimental $C_{x,\mathrm{m}}^{\mathrm{II}}$ values (Table 2) were converted to $C_{V,\mathrm{m}}^{\mathrm{II}}$ by means of eq 6 with eq 5 for the cell expansion and the vapor-pressure fit used for $(\partial p/\partial T)_{\mathrm{sat}}$,

$$C_{V,\mathrm{m}}^{\mathrm{II}} = C_{x,\mathrm{m}}^{\mathrm{II}} - T/n\{(\partial V_x/\partial T)_x(\partial p/\partial T)_{\mathrm{sat}}\} \qquad (6)$$

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

$$(\partial^2 \mu/\partial T^2)_{\mathrm{sat}}/(\mathrm{J\cdot K^{-2}\cdot mol^{-1}}) = \sum_{i=0}^{n} b_i(1 - T/T_{\mathrm{c}})^i \qquad (7)$$

Table 2. Two-Phase (Liquid + Vapor) Heat Capacities ($R = 8.314\ 51\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

Benzenamine

T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$			T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$		
	m/g = 0.009 558 $V_c{}^a$ = 0.052 19	m/g = 0.015 291 $V_c{}^a$ = 0.052 17	m/g = 0.021 870 $V_c{}^a$ = 0.052 19		m/g = 0.009 558 $V_c{}^a$ = 0.052 19	m/g = 0.015 291 $V_c{}^a$ = 0.052 17	m/g = 0.021 870 $V_c{}^a$ = 0.052 19
315.0	23.8	22.9	23.2	515.0	32.0	30.1	29.4
335.0	24.2	23.5	23.7	535.0	33.3	31.0	30.1
355.0	24.6	24.2	24.2	555.0	34.7	32.1	30.9
375.0	25.4	24.5	24.8	575.0	36.1	32.5	31.6
395.0	26.1	25.3	25.4	595.0	37.6	33.6	32.2
415.0	26.8	26.0	25.9	615.0	39.0	34.9	32.7
435.0	27.7	26.7	26.6	635.0	40.9	35.0	33.8
455.0	28.7	27.6	27.3	655.0	42.3	37.2	34.8
475.0	29.8	28.3	28.0	675.0	43.7	39.5	37.1
495.0	30.6	29.2	28.7				

Butylbenzene

T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$			T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$		
	m/g = 0.010 366 $V_c{}^a$ = 0.052 19	m/g = 0.014 755 $V_c{}^a$ = 0.052 17	m/g = 0.020 679 $V_c{}^a$ = 0.052 19		m/g = 0.010 366 $V_c{}^a$ = 0.052 19	m/g = 0.014 755 $V_c{}^a$ = 0.052 17	m/g = 0.020 679 $V_c{}^a$ = 0.052 19
315.0	30.3	30.3	30.0	495.0	42.4	41.9	41.4
335.0	31.2	31.4	31.2	515.0	44.4	43.5	42.7
355.0	32.6	32.4	32.5	535.0	46.6	44.9	44.0
375.0	33.9	33.6	33.7	555.0	48.4	47.0	45.1
395.0	34.8	35.1	35.1	575.0	50.5	47.5	46.5
415.0	36.2	36.3	36.4	595.0	52.2	49.5	47.5
435.0	37.7	37.5	37.5	615.0	55.0	51.4	49.4
455.0	39.2	38.9	38.9	635.0	56.7	53.9	51.8
475.0	40.9	40.4	40.2				

sec-Butylbenzene

T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$			T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$		
	m/g = 0.011 164 $V_c{}^a$ = 0.052 17	m/g = 0.015 516 $V_c{}^a$ = 0.052 17	m/g = 0.019 848 $V_c{}^a$ = 0.052 19		m/g = 0.011 164 $V_c{}^a$ = 0.052 17	m/g = 0.015 516 $V_c{}^a$ = 0.052 17	m/g = 0.019 848 $V_c{}^a$ = 0.052 19
315.0	30.7	30.8	29.9	495.0	44.4	42.3	41.5
335.0	32.2	31.9	31.1	515.0	45.8	43.9	42.9
355.0	33.2	33.0	32.4	535.0	47.5	45.2	43.9
375.0	34.7	34.0	33.4	555.0	49.1	46.2	45.4
395.0	36.1	35.2	34.6	575.0	51.2	48.2	46.8
415.0	37.5	36.5	36.3	595.0	53.0	49.8	48.4
435.0	39.3	38.1	37.8	615.0	54.7	52.0	50.6
455.0	40.9	39.3	39.1	635.0	60.5	57.2	53.9
475.0	42.3	40.8	40.4				

tert-Butylbenzene

T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$			T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$		
	m/g = 0.011 567 $V_c{}^a$ = 0.052 19	m/g = 0.016 003 $V_c{}^a$ = 0.052 17	m/g = 0.021 290 $V_c{}^a$ = 0.052 19		m/g = 0.011 567 $V_c{}^a$ = 0.052 19	m/g = 0.016 003 $V_c{}^a$ = 0.052 17	m/g = 0.021 290 $V_c{}^a$ = 0.052 19
315.0	30.3	30.1	30.0	475.0	41.8	40.6	40.1
335.0	31.6	31.2	31.2	495.0	43.2	42.1	41.6
355.0	33.0	32.3	32.6	515.0	45.2	43.3	42.8
375.0	34.2	33.8	33.8	535.0	46.7	44.8	43.8
395.0	35.7	35.2	35.1	555.0	48.7	46.4	45.0
415.0	37.2	36.4	36.4	575.0	50.0	47.7	46.9
435.0	38.6	38.0	37.6	595.0	52.6	49.4	48.2
455.0	40.3	39.3	38.9	615.0	55.3	52.2	50.5

T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$	T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$	T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$	T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$
2,2-Dimethylbutanoic Acid[b]				2-Butyl-2-ethyl-1,3-propanediol[d]			
315.0	28.5	435.0	38.2	$\Delta^{\mathrm{l}}_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(317.3\ \mathrm{K}) = (20.8 \pm 0.4)\ \mathrm{kJ \cdot mol^{-1}}$			
335.0	29.9	455.0	39.7	340.0	51.2	440.0	59.5
355.0	31.4	475.0	41.2	360.0	53.1	460.0	60.3
375.0	33.1	495.0	42.7	380.0	55.2	480.0	61.5
395.0	34.7	515.0	44.2	400.0	56.7	500.0	62.3
415.0	36.5	535.0	45.5	420.0	58.1		
Tridecafluoroheptanoic acid[c]				1-Chloro-2-propanol[e]			
$\Delta^{\mathrm{l}}_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(308.7\ \mathrm{K}) = (16.3 \pm 0.2)\ \mathrm{kJ \cdot mol^{-1}}$				315.0	24.8	375.0	26.6
330.0	54.2	430.0	65.1	335.0	25.5	395.0	27.2
350.0	56.2	450.0	67.8	355.0	26.1	415.0	27.8
370.0	59.0	470.0	69.9	2,2,4-Trimethyl-1,3-pentanediol[f]			
390.0	61.1	490.0	71.7	$\Delta^{\mathrm{l}}_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(328.3\ \mathrm{K}) = (24.2 \pm 0.5)\ \mathrm{kJ \cdot mol^{-1}}$			
410.0	62.9	510.0	74.2	350.0	46.9	410.0	52.5
				370.0	49.1	430.0	53.8
				390.0	51.0	450.0	54.7

[a] Volume of cell (V_c) is given in cubic centimeters for 298.15 K. [b] Measurements made on a sample of mass 0.020 811 g in a cell of volume 0.0522 cm^3. [c] Measurements made on a sample of mass 0.022 273 g in a cell of volume 0.0522 cm^3. [d] Measurements made on a sample of mass 0.020 018 g in a cell of volume 0.0522 cm^3. [e] Measurements made on a sample of mass 0.015 262 g in a cell of volume 0.0522 cm^3. [f] Measurements made on a sample of mass 0.020 180 g in a cell of volume 0.0522 cm^3.

Table 3. Densities and Temperatures Used To Define the Two-Phase Dome near T_c and Shown in Figure 2

ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K
Benzenamine		Butylbenzene	
162.2	684.0	195.0	658.2
198.0	696.0	236.3	660.2
243.8	701.0	277.6	660.5
291.4	704.3	335.5	659.7
318.0	704.8	389.2	649.8
335.5	705.0		
410.0	704.0		
440.7	697.0		
491.2	688.2		
sec-Butylbenzene		*tert*-Butylbenzene	
176.5	647.0	158.4	638.3
210.2	650.4	217.8	646.9
241.3	652.0	249.9	647.5
292.1	652.0	301.4	647.1
332.8	651.5	332.3	646.7
373.7	646.8	401.1	638.0

For compounds where sufficient information was available to evaluate reliably $(\partial^2\mu/\partial T^2)_{\mathrm{sat}}$ (e.g., benzene[30] and toluene[31]), four terms (i.e., expansion to $n = 3$) were required to represent the function.[13] Thus, four terms were used in this research. Estimates of liquid-phase molar volumes $V_{\mathrm{m}}(\mathrm{l})$ for each compound were made using the equations listed in the footnotes of Table 4. In earlier work in this project, the estimates were made with the extended corresponding-states equation of Riedel[32] as formulated by Hales and Townsend[25]

$$(\rho/\rho_c) = 1.0 + 0.85Y + (1.6916 + 0.9846\omega)Y^{1/3} \quad (8)$$

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

$$\rho = \rho_c + A(1 - T_r)^{1/3} + B(1 - T_r)^{2/3} + C(1 - T_r) + \ldots \quad (9)$$

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.[14-16]

The above procedures were not used for both diols (2-butyl-2-ethyl-1,3-propanediol and 2,2,4-trimethyl-1,3-pentanediol) and 1-chloro-2-propanol. All three compounds decomposed well below the critical region, measured vapor pressures covered a narrow range of temperatures (Table 1B), and the measured $C^{\mathrm{II}}_{x,\mathrm{m}}$ values (Table 2) were virtually independent of cell filling. The absence of measured critical properties precluded application of the methodology used in the previous section. The Antoine equation (eq 2) was fitted to the measured vapor pressures (Table 1B). For both diols, estimated critical temperatures and critical densities were used in the derivation of the parameters in eq 9 (see footnotes of Table 4). For 1-chloro-2-propanol, no fit to eq 9 was attempted because of the narrow temperature range of the measured densities.

Derived Results. Tables 5 and 6 list the parameters derived using the procedures outlined above. Details of the fits to the vapor-pressure results are given in Table 1. Details of the fits of eq 9 to the measured liquid-phase densities are given in column 3 of Table 4 for each compound (the actual equations are listed in the footnotes).

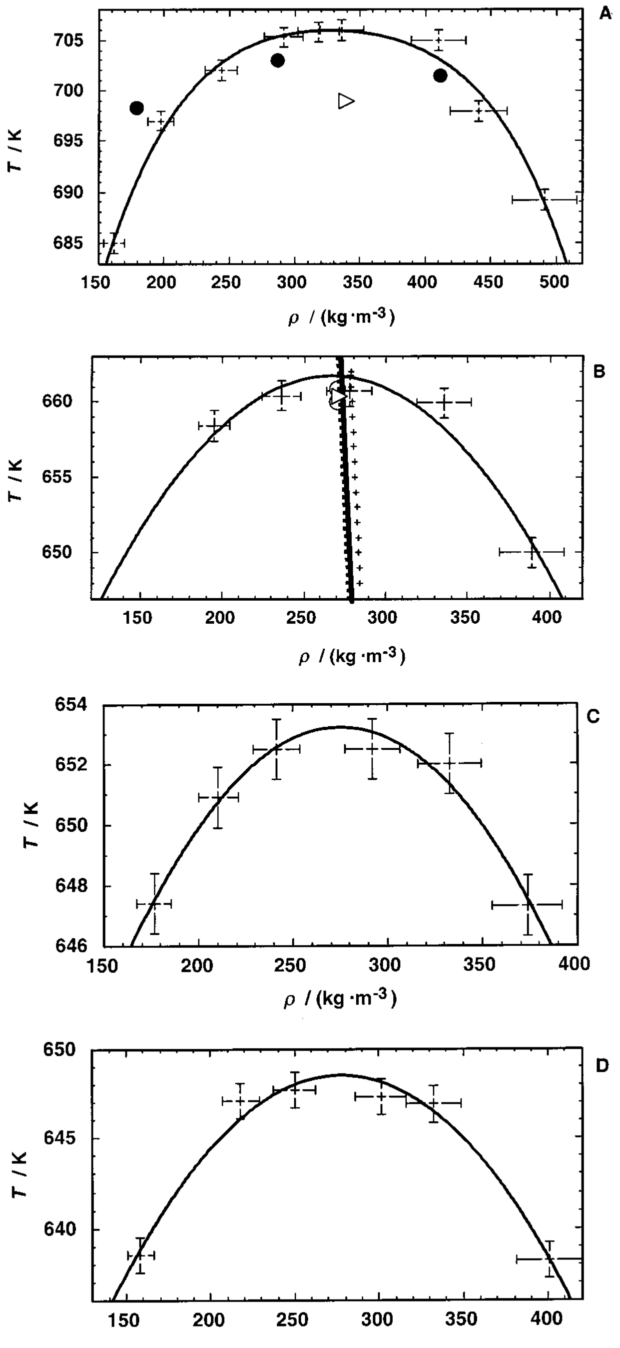

Figure 2. Vapor–liquid coexistence in the region of the critical point. In each part of the figure, the curves are drawn as an aid to the eye and do not represent any theoretically valid equation. The crosses span the range of uncertainty. (A) Benzenamine: (triangle pointing right) Ambrose;[38,39] (●) results from the measurements of heat capacity, i.e., long runs where significant decomposition appeared to occur. (B) Butylbenzene: (triangle pointing right) the critical temperatures and critical densities listed by Tsonopoulos and Ambrose;[92] (○) Simon;[93] (+) the rectilinear diameter line of Massart;[96] (- - -) the rectilinear diameter line of Simon.[93] (C) *sec*-Butylbenzene. (D) *tert*-Butylbenzene.

For benzenamine, and the three butylbenzenes, values of $C^{\mathrm{II}}_{V,\mathrm{m}}(\rho{=}\rho_{\mathrm{sat}})$ were derived from the parameters listed in Table 5, and corresponding $C_{\mathrm{sat,m}}$ values were obtained using the equation

$$C^{\mathrm{II}}_{V,\mathrm{m}}(\rho{=}\rho_{\mathrm{sat}}) = n[C_{\mathrm{sat,m}} - \{T(\partial p/\partial T)_{\mathrm{sat}}(\mathrm{d}V_{\mathrm{m}}(\mathrm{l})/\mathrm{d}T)\}] \quad (10)$$

The results for $C_{\mathrm{sat,m}}$ are reported in Table 7. The estimated uncertainty in these values is 1%.

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

T/K	ρ/(kg·m^{-3})	100($\rho - \rho_{calc}$)/ρ	T/K	ρ(kg·m^{-3})	100($\rho - \rho_{calc}$)/ρ
	Benzenamine[b]			Butylbenzene[c]	
323.136	994.7	0.03	323.136	835.5	0.04
348.131	973.0	0.00	348.131	815.0	−0.01
373.124	950.6	−0.04	373.124	794.1	−0.04
398.118	928.2	−0.03	398.118	772.7	−0.05
423.113	905.1	−0.02	423.113	751.0	0.01
448.111	881.4	0.02	448.111	728.1	0.03
473.111	856.9	0.06	473.111	703.8	0.03
498.108	830.7	0.04	498.108	678.2	0.04
523.110	802.7	−0.06	523.110	650.1	−0.05
	sec-Butylbenzene[d]			*tert*-Butylbenzene[e]	
323.136	837.1	0.02	323.136	841.44	0.04
348.131	816.9	0.01	348.131	820.33	−0.02
373.124	795.7	−0.04	373.124	798.86	−0.06
398.118	774.4	−0.02	398.118	777.40	−0.01
423.113	751.9	−0.03	423.113	755.26	0.07
448.111	728.8	0.03	448.111	731.23	0.02
473.111	704.1	0.04	473.111	705.85	−0.04
498.108	677.6	0.03			
523.110	648.7	−0.04			
	2,2-Dimethylbutanoic acid[f]			Tridecafluoroheptanoic acid[g]	
323.136	899.3	−0.01	323.136	1729	0.00
348.131	877.6	0.03	348.131	1675	0.00
373.124	854.8	−0.04	373.124	1620	0.00
398.118	832.6	0.01	398.118	1562	0.00
423.113	809.3	−0.01	423.113	1501	0.00
	2-Butyl-2-ethyl-1,3-propanediol[h]			1-Chloro-2-propanol[i]	
323.149	926.8	0.02	323.136	1076	
348.150	909.1	0.00	348.131	1048	
373.150	890.7	−0.03	373.124	1018	
398.148	871.9	−0.04			
423.149	853.0	0.03			
448.253	832.5	0.01			
473.150	811.5	0.03			
498.152	788.9	−0.03			
	2,2,4-Trimethyl-1,3-pentanediol[j]				
348.149	907.5	0.03			
373.150	888.9	−0.02			
398.149	870.0	0.01			
423.149	849.9	0.04			
448.152	827.8	−0.02			
473.149	805.2	0.04			
498.149	780.1	−0.01			

[a] ρ_{calc} values were calculated using eq 9 and the parameters listed below. [b] $\rho_{calc} = 317.3 + 716.6(1 - T/705)^{1/3} - 165.1(1 - T/705)^{2/3} + 374.2(1 - T/705)$. [c] $\rho_{calc} = 268.9 + 589.3(1 - T/660.5)^{1/3} - 70.3(1 - T/660.5)^{2/3} + 274.3(1 - T/660.5)$. [d] $\rho_{calc} = 273.7 + 573.0(1 - T/652.5)^{1/3} - 9.56(1 - T/652.5)^{2/3} + 224.0(1 - T/652.5)$. [e] $\rho_{calc} = 277.1 + 641.7(1 - T/647.5)^{1/3} - 187.8(1 - T/647.5)^{2/3} + 344.9(1 - T/647.5)$. [f] $\rho_{calc} = 272.4 + 1055.3(1 - T/655)^{1/3} - 1062.1(1 - T/655)^{2/3} + 909.4(1 - T/655)$. [g] $\rho_{calc} = 508.8 + 1580.8(1 - T/583)^{1/3} - 662.7(1 - T/583)^{2/3} + 894.7(1 - T/583)$. [h] $\rho_{calc} = 287.5 + 365.5(1 - T/755)^{1/3} + 604.1(1 - T/755)^{2/3} - 140.8(1 - T/755)$. [i] No fit was attempted because of the narrow temperature range of the measured densities. [j] $\rho_{calc} = 277.0 + 219.3(1 - T/720)^{1/3} + 1164.5(1 - T/720)^{2/3} - 571.7(1 - T/720)$.

Table 5. Parameters for Eqs 1 and 7, Critical Constants, and Acentric Factors[a]

	Benzenamine				Butylbenzene		
A	−8.487 12	b_0	−0.281 86	A	−8.819 81	b_0	−0.505 59
B	3.356 34	b_1	−1.113 72	B	3.696 73	b_1	−1.148 39
C	−4.105 01	b_2	2.537 31	C	−4.535 72	b_2	2.634 83
D	−4.000 20	b_3	−2.927 39	D	−2.793 51	b_3	−2.873 43
T_c	705 K	p_c	5630 kPa	T_c	660.5 K	p_c	2990 kPa
ρ_c	317 kg·m^{-3}	ω	0.3691	ρ_c	269 kg·m^{-3}	ω	0.4077
	sec-Butylbenzene				*tert*-Butylbenzene		
A	−8.282 92	b_0	−0.543 93	A	−7.443 55	b_0	−0.527 60
B	2.848 74	b_1	−0.995 22	B	1.194 24	b_1	−1.191 85
C	−3.634 12	b_2	2.587 09	C	−2.313 54	b_2	3.058 08
D	−3.182 81	b_3	−3.161 03	D	−4.331 78	b_3	−3.361 07
T_c	652.5 K	p_c	3025 kPa	T_c	647.5 K	p_c	2900 kPa
ρ_c	274 kg·m^{-3}	ω	0.3672	ρ_c	277 kg·m^{-3}	ω	0.3410
	2,2-Dimethylbutanoic Acid				Tridecafluoroheptanoic Acid		
A	−8.181 28			A	−12.073 51		
B	1.136 24			B	7.496 20		
C	−6.632 27			C	−15.942 12		
D	−1.686 54			D	3.908 31		
T_c	655 K	p_c	3850 kPa	T_c	583 K	p_c	2075 kPa
ρ_c	272 kg·m^{-3}	ω	0.6123	ρ_c	509 kg·m^{-3}	ω	0.9647

[a] The parameters listed in this table are those derived from the fitting procedures. Table 10 lists “recommended” critical parameters.

Table 6. Antoine Equation Coefficients

2-Butyl-2-ethyl-1,3-propanediol		1-Chloro-2-propanol	
P_{ref}/kPa	1	P_{ref}/kPa	1
A	6.171 13	A	6.408 77
B	−1614.866	B	−1425.326
C	−149.393	C	−75.5142
range[a]/K	424 to 523	range[a]/K	308 to 399
2,2,4-Trimethyl-1,3-pentanediol			
P_{ref}/kPa	1		
A	6.156 13		
B	−1524.885		
C	−135.565		
range[a]/K	396 to 489		

[a] Temperature range of the vapor pressures used in the fit.

Table 7. Values of $C_{sat,m}/R$ (R = 8.314 51 J·K^{-1}·mol^{-1})

T/K	$C_{sat,m}/R$	T/K	$C_{sat,m}/R$	T/K	$C_{sat,m}/R$	T/K	$C_{sat,m}/R$
	Benzenamine				Butylbenzene		
300.0	23.1	520.0	29.2	300.0	29.4	480.0	40.1
320.0	23.5	540.0	29.9	320.0	30.5	500.0	41.4
340.0	23.9	560.0	30.5	340.0	31.5	520.0	42.6
360.0	24.4	580.0	31.0	360.0	32.7	540.0	43.8
380.0	24.9	600.0	31.6	380.0	33.8	560.0	44.9
400.0	25.4	620.0	32.2	400.0	35.0	580.0	46.1
420.0	26.0	640.0	32.9	420.0	36.3	600.0	47.4
440.0	26.6	660.0	34.1	440.0	37.6	620.0	49.4
460.0	27.2	680.0	37.4	460.0	38.8	640.0	54
480.0	27.9	700.0	61				
500.0	28.5						
	sec-Butylbenzene				*tert*-Butylbenzene		
300.0	29.4	480.0	40.1	300.0	29.1	480.0	40.7
320.0	30.3	500.0	41.5	320.0	30.2	500.0	42.2
340.0	31.3	520.0	43.0	340.0	31.3	520.0	43.5
360.0	32.4	540.0	44.4	360.0	32.5	540.0	44.8
380.0	33.5	560.0	45.8	380.0	33.7	560.0	46.0
400.0	34.7	580.0	47.3	400.0	35.1	580.0	47.1
420.0	36.0	600.0	49.1	420.0	36.4	600.0	48.4
440.0	37.3	620.0	51.8	440.0	37.9	620.0	50.6
460.0	38.7	640.0	60	460.0	39.3	640.0	61

Enthalpies of vaporization $\Delta_l^g H_m$ were derived from the Wagner- or Antoine-equation fits using the Clapeyron equation:

$$dp/dT = \Delta_l^g H_m/(T\Delta_l^g V_m) \tag{11}$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. For benzenamine, the butylbenzenes, 2,2-dimethylbutanoic acid, and tridecafluoroheptanoic acid, estimates of the liquid-phase volumes were made using eq 9 and the parameters given in the footnotes of Table 4. Vapor-phase volumes were calculated with the virial equation of state truncated at the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl,[33] and third virial coefficients were estimated also with the corresponding-states method of Orbey and Vera.[34] This

Table 8. Enthalpies of Vaporization[a]

T/K	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$/kJ·mol^{-1}	T/K	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$/kJ·mol^{-1}
	A. Wagner and Clapeyron Equations		
	Benzenamine		
298.15^{b}	55.87 ± 0.22	440.0	45.17 ± 0.23
300.0^{b}	55.72 ± 0.22	460.0	43.72 ± 0.32
320.0^{b}	54.08 ± 0.20	480.0	42.23 ± 0.42
340.0^{b}	52.50 ± 0.18	500.0	40.69 ± 0.55
360.0	50.97 ± 0.17	520.0^{b}	39.09 ± 0.68
380.0	49.49 ± 0.17	540.0^{b}	37.43 ± 0.85
400.0	48.04 ± 0.17	560.0^{b}	35.7 ± 1.1
420.0	46.61 ± 0.20		
	Butylbenzene		
290.0^{b}	51.42 ± 0.20	430.0	42.07 ± 0.28
298.15^{b}	50.85 ± 0.18	450.0	40.64 ± 0.38
310.0^{b}	50.05 ± 0.18	470.0	39.13 ± 0.50
330.0^{b}	48.71 ± 0.17	490.0	37.52 ± 0.65
350.0	47.39 ± 0.17	510.0^{b}	35.82 ± 0.83
370.0	46.09 ± 0.15	530.0^{b}	34.0 ± 1.0
390.0	44.78 ± 0.17	550.0^{b}	32.0 ± 1.3
410.0	43.45 ± 0.22		
	sec-Butylbenzene		
280.0^{b}	49.71 ± 0.18	420.0	40.60 ± 0.27
298.15^{b}	48.47 ± 0.17	440.0	39.23 ± 0.37
300.0^{b}	48.34 ± 0.17	460.0	37.77 ± 0.48
320.0^{b}	47.02 ± 0.17	480.0	36.22 ± 0.63
340.0	45.73 ± 0.15	500.0^{b}	34.55 ± 0.80
360.0	44.47 ± 0.15	520.0^{b}	32.8 ± 1.0
380.0	43.20 ± 0.17	540.0^{b}	30.8 ± 1.2
400.0	41.92 ± 0.20		
	tert-Butylbenzene		
280.0^{b}	49.55 ± 0.18	420.0	39.92 ± 0.28
298.15^{b}	48.19 ± 0.17	440.0	38.49 ± 0.38
300.0^{b}	48.05 ± 0.17	460.0	36.97 ± 0.52
320.0^{b}	46.62 ± 0.17	480.0	35.34 ± 0.68
340.0	45.26 ± 0.15	500.0^{b}	33.57 ± 0.85
360.0	43.93 ± 0.15	520.0^{b}	31.6 ± 1.1
380.0	42.60 ± 0.17	540.0^{b}	29.5 ± 1.3
400.0	41.28 ± 0.22		
	2,2-Dimethylbutanoic acid		
298.15^{b}	65.67 ± 0.35	430.0	53.49 ± 0.28
310.0^{b}	64.65 ± 0.33	450.0	50.00 ± 0.38
330.0^{b}	62.91 ± 0.30	470.0	48.73 ± 0.52
350.0^{b}	61.16 ± 0.27	490.0	45.99 ± 0.70
370.0	59.37 ± 0.25	510.0^{b}	42.99 ± 0.93
390.0	57.57 ± 0.23	530.0^{b}	39.7 ± 1.2
410.0	54.55 ± 0.25	550.0^{b}	36.1 ± 1.5
	Tridecafluoroheptanoic acid		
298.15^{b,c}	69.97 ± 0.42	430.0	52.24 ± 0.47
310.0^{b,c}	68.70 ± 0.40	450.0	48.70 ± 0.67
330.0^{b}	66.42 ± 0.37	470.0	44.91 ± 0.93
350.0^{b}	63.98 ± 0.33	490.0^{b}	40.9 ± 1.3
370.0	61.38 ± 0.30	510.0^{b}	36.6 ± 1.7
390.0	58.57 ± 0.30	530.0^{b}	32.1 ± 2.2
410.0	55.53 ± 0.33		

T/K	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$/kJ·mol^{-1}	T/K	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$/kJ·mol^{-1}
	B. Antoine and Clapeyron Equations		
	2-Butyl-2-ethyl-1,3-propanediol		
298.15^{b,c}	124 ± 22	460.0	67.2 ± 0.3
360.0^{b}	90.3 ± 0.7	480.0	64.2 ± 0.4
380.0^{b}	83.9 ± 0.5	500.0	61.4 ± 0.6
400.0^{b}	78.7 ± 0.4	520.0	58.7 ± 0.8
420.0	74.3 ± 0.3	540.0^{b}	56 ± 1
440.0	70.5 ± 0.3		
	1-Chloro-2-propanol		
298.15^{b}	49 ± 3	380.0	42.2 ± 1.9
300.0^{b}	49 ± 3	400.0^{b}	40.9 ± 1.9
320.0	46.7 ± 2.5	420.0^{b}	39.8 ± 1.9
340.0	45.0 ± 2.2	440.0^{b}	38.6 ± 1.9
360.0	43.5 ± 2.0		
	2,2,4-Trimethyl-1,3-pentanediol		
298.15^{b,c}	98 ± 12	440.0	60.3 ± 1.7
340.0^{b}	81 ± 5	460.0	57.6 ± 1.6
360.0^{b}	75 ± 3	480.0	55.0 ± 1.6
380.0^{b}	71 ± 3	500.0^{b}	53 ± 2
400.0	66.6 ± 2.1	520.0^{b}	50 ± 2
420.0	63.3 ± 1.8	540.0^{b}	47 ± 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 equation. [c] The value at this temperature is for the supercooled liquid.

formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene and toluene.[24] 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 8. For $p > 1$ bar the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization.

For those compounds where the Antoine equation was used to represent the measured vapor pressures (both diols and 1-chloro-2-propanol), enthalpies of vaporization were determined as follows. Second virial coefficients were estimated with the correlation of Scott et al.[35] Since enthalpies of vaporization were not derived for pressures greater than 1 bar, third virials were neglected. For the diols, liquid-phase volumes were derived using the equations listed in the footnotes of Table 4. For 1-chloro-2-propanol, liquid-phase volumes were derived using the density at 298.15 K and an average coefficient of expansion derived from the three measured densities. For these three compounds the derived enthalpies of vaporization are reported in Table 8B. Uncertainties in both the liquid-phase molar volumes and virial coefficients were assumed to be 20%.

Solubility parameters are listed in Table 9. The solubility parameter is defined as $\delta = [(\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}} - RT)\rho]^{1/2}$, where $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ is the enthalpy of vaporization at 298.15 K (or the

Table 9. Solubility Parameters, δ[a]

ρ/mol·m^{-3}	$\Delta_l^g U_m$/J·mol^{-1}	$10^{-4}\delta$/(J·m^{-3})$^{1/2}$
	Benzenamine	
10903	53390	2.41
	Butylbenzene	
6431.4	48370	1.76
	sec-Butylbenzene	
6380.7	45990	1.71
	tert-Butylbenzene	
6415.7	45710	1.71
	2,2-Dimethylbutanoic acid	
7931.0	62610	2.23
	Tridecafluoroheptanoic acid	
4829.8	66270	1.79
	2-Butyl-2-ethyl-1,3-propanediol	
5807.2	110960	2.54
	1-Chloro-2-propanol	
11677	46420	2.33
	2,2,4-Trimethyl-1,3-pentanediol	
6298.6	83070	2.29

[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. $\Delta_l^g U_m = (\Delta_l^g H_m - RT)$ was 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 8. The melting points were as follows: tridecafluoroheptanoic acid, 308.7 K; 2-butyl-2-ethyl-1,3-propanediol, 317.3 K; 2,2,4-trimethyl-1,3-pentanediol, 328.3 K.

Table 10. "Recommended" Critical Properties[a]

compd	T_c/K	p_c/kPa	ρ_c/kg·m^{-3}
benzenamine	705 ± 1	5630 ± 200	317 ± 9
butylbenzene	660.5 ± 1	2990 ± 200	269 ± 9
sec-butylbenzene	652.5 ± 1	3025 ± 200	274 ± 9
tert-butylbenzene	647.5 ± 1	2900 ± 200	277 ± 9
2,2-dimethylbutanoic acid	655 ± 15	3850 ± 500	272 ± 15
tridecafluoroheptanoic acid	583 ± 15	2075 ± 500	509 ± 15
2-butyl-2-ethyl-1,3-propanediol	690 ± 15	2000 ± 500	290 ± 15
2,2,4-trimethyl-1,3-pentanediol	720 ± 15		280 ± 15

[a] For benzenamine and the three butylbenzenes, the reported critical temperatures and critical densities and their uncertainty intervals were obtained from the DSC measurements. For the remaining compounds, the critical temperatures are estimates. The critical pressures listed were determined using the fitting procedures detailed in the text.

melting point if above 298.15 K), R is the gas constant, $T = 298.15$ K (or the melting point), and $\rho =$ the saturation liquid density at 298.15 K (or the melting point). Table 10 lists "recommended" values for the critical properties for eight of the nine compounds studied. The exception is 1-chloro-2-propanol, for which no values are recommended in this research.

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.[36,37] The 1985 reference was the first "hard-copy" version of the 801 Database available to the general public. The 1996 reference was the version available to the general public using computer-searching techniques during the 1996 calendar year when the original version of this report was written.

Comparison with Literature Values. Benzenamine. Literature references to the critical properties of benzenamine, for example, refs 38 and 39, can be traced to the work reported to the Academie des Sciences Paris on January 20, 1902, by M. Sarrau. Monsieur Sarrau reported a note from Mademoiselle Pu.-A Guye and E. Mallet[40] on the critical constants of six "complex organic molecules" including benzenamine. Results on duplicate samples of benzenamine were reported: $T_c = 698.8$ K and 698.5 K, respectively, with corresponding critical pressures $p_c = 5309$ kPa and $p_c = 5299$ kPa. No appreciable polymerization at the critical point was observed. As noted above, although the Wagner equation fit (see Table 1A) for benzenamine does not show it and fast-scan DSC critical-region results were obtained (see Table 3), the increase in ΔT (see Table 1) above the normal boiling point indicates that slow decomposition was occurring in the sample. A critical temperature $T_c = (705 \pm 1)$ K was obtained in this research (Table 3 and Figure 2) with a corresponding critical pressure of (5630 ± 200) kPa derived from the fitting procedures. A critical density of (317 ± 9) kg·m^{-3} is recommended (see Table 10).

The vapor-pressure literature for benzenamine is extensive, spanning approximately one century. The earliest references found were those of Ramsay and Young in 1885,[41] Neubeck in 1887,[42] and Kahlbaum in 1898.[43] In addition, a further 19 papers listing measured vapor pressures were obtained in a search of the literature during this research.[44−62]

Figure 3 compares the literature results for benzenamine with values obtained using the Wagner vapor-pressure equation (eq 1) and the parameters listed in Table 1. In Figure 3A, the solid curve represents the vapor-pressure equation derived in an API (American Petroleum Institute) report,[63] the dotted curve results from use of the 1984 version of the DIPPR Project 801 Database,[36] and the dashed curve results from use of the DIPPR 801 1995 version of the vapor-pressure equation.[37] Also represented in Figure 3A are the high-pressure (above 154 kPa) results of Lastovtsev[47] and Lee et al.[62] It should be noted that the large negative deviations of the API representation of the vapor pressure below 350 K are only supported by the results of Gurevich and Sigalovskaya[46] and Gopal and Rizvi[58] (see Figure 3B). The author of the API report lists neither of these two references as being considered in the derivation of their vapor-pressure equation. Figure 3B compares results of this research with those from the following references: Gurevich and Sigalovskaya;[46] Röck;[50] Danov and Shinyaeva;[55] Pannier and Abello;[56] Gopal and Rizvi;[58] Maher and Smith;[59] Rowley and Powell.[61] Most of the results represented in Figure 3B are outside the temperature range of measurements reported in this research (Table 1). However, there is virtually no agreement between each of the references and the possible exception of the results of Röck[50] and Maher and Smith.[59] Note in Figure 3B that the abscissa covers the range +35% to −70% deviation $[100(p - p_{\mathrm{Wagner}})/p]$. Figure 3C (the abscissa spans the range ±10% deviation) shows the results of Neubeck,[42] Gould et al.,[48] Dreisbach and Shrader,[49] and McDonald et al.[53] Figure 3D (the abscissa spans the range ±3% deviation) shows the remaining references.[41,43−45,51,52,55,57] Not included in Figure 3D is the value listed by Kahlbaum for 331 K (−6.7% deviation), which may be a typographical error.

The literature on the density of benzenamine is even more extensive than that for the vapor pressures, spanning well over a century. It would be impossible to list all the measured values extracted in the literature search for this project. A decision was made to compare with only those

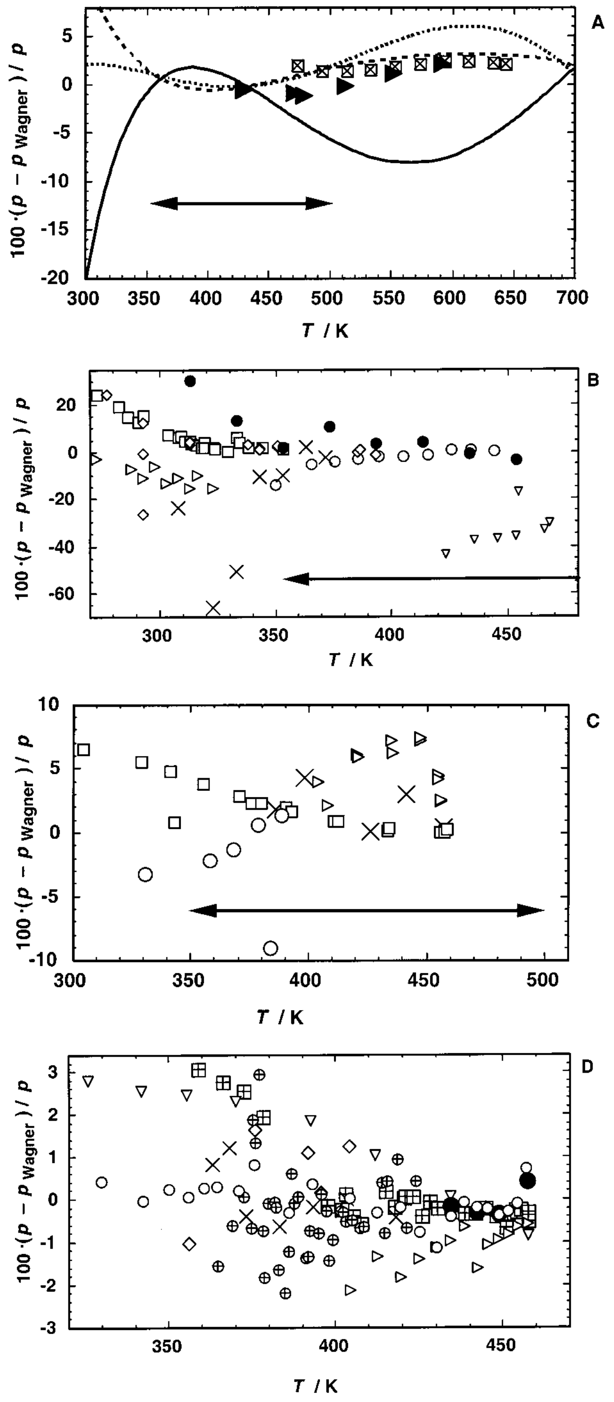

Figure 3. Comparison of literature vapor-pressure measurements for benzenamine with those obtained using the Wagner equation (eq 1) and the parameters listed in Table 5. The doubled-headed arrow represents the range of the vapor-pressure measurements reported in this research (see Table 1). (A) (—) results from the API Technical Report (Kudchadker[63]); (· · ·) results using the DIPPR Project 801 Database 1984 version of the vapor-pressure equation;[36] (- - -) results using the DIPPR Project 801 Database 1995 version of the vapor-pressure equation;[37] (× in a box) Lastovtsev;[47] (solid triangle pointing right) Lee et al.[62] (B) (triangle pointing right) Gurevich and Sigalovskaya;[46] (□) Röck;[50] (●) Danov and Shinyaeva;[55] (▽) Pannier and Abello;[56] (×) Gopal and Rizvi;[58] (◇) Maher and Smith;[59] (○) Rowley and Powell.[61] (C) (triangle pointing right) Neubeck;[42] (○) Gould et al.;[48] (×) Dreisbach and Shrader;[49] (□) McDonald et al.[53] (D) (⊞) Ramsay and Young;[41] (○) Kahlbaum;[43] (triangle pointing right) Beckmann and Liesche;[44] (+ in a circle) Garrick;[45] (×) Crützen et al.;[51] (◇) Böhme et al.;[52] (▽) Hatton et al.;[54] (●) Stadnicki.[57]

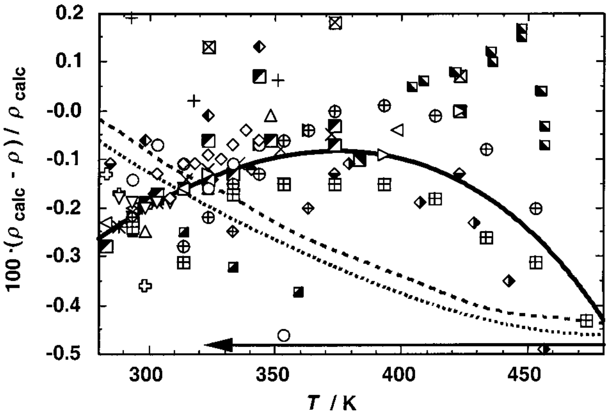

Figure 4. Comparison of literature density measurements for benzenamine with those obtained using eq 12. The dotted curve, the dashed curve, and the solid curve represent the equations for the saturation liquid density for benzenamine given in the DIPPR Project 801 Database 1984 version,[36] the DIPPR Project 801 Database 1995 version,[37] and the API Technical Report (Kudchadker[63]), respectively. (× in a box) Kopp;[64] (diamond with solid bottom) Thorpe;[65] (◩) Neubeck;[42] (✙) Perkin;[66] (+) Dutoit, and Friederich;[67] (diamond with solid top) Livingston et al.;[68] (×) Tyrer;[69] (◨) Bramley, 1916a;[70] (triangle pointing left) Bramley, 1916b;[71] (diamond with solid left side) Jaeger;[72] (◩) Bingham et al.;[73] (triangle pointing right) Buehler et al.;[74] (∗) Timmermans and Hennaut-Roland;[75] (diamond with solid right side) Friend and Hargreaves;[76] (◪) Vogel;[77] (▽) Hatem;[78] (+ in a circle) Hough et al.;[79] (+ in a diamond) Kovalenko and Trifonov;[80] (⊞) Costello and Bowden;[81] (△) Fialkov et al.;[82] (○) Neronov and Chviruk;[83] (◇) Guinda et al.[84]

studies that covered a range of temperature (at least 50 K). Even then, the reference list is extensive (see Figure 4 caption).[64−84] Figure 4 compares values for the saturated liquid-phase density of benzenamine found in the literature[64−84] with values calculated using eq 12 derived from a fit of the measurements reported in Table 4.

$$\rho/\mathrm{kg{\cdot}m^{-3}} = 317.3 - 716.6(1 - T/705)^{1/3} - 165.1(1 - T/705)^{2/3} + 374.2(1 - T/705) \quad (12)$$

In Figure 4 the dotted curve, the dashed curve, and the solid curve represent the equations for the saturation liquid density for benzenamine given in the DIPPR Project 801 Database 1984 version,[36] the DIPPR Project 801 Database 1995 version,[37] and the API Technical Report,[63] respectively. While the API equation represents the bulk of the literature values well, the DIPPR 801 Project Database representations do not. None of the sets of values for the saturation liquid density across a temperature range shown in Figure 4 are in accord with the measurements reported in this research. No details are reported of the purities of the samples except by Timmermans and Hennaut-Roland.[75]

Liquid-phase heat-capacity values for benzenamine abound, particularly in the pre-1940 literature. In an attempt to restrict the literature references, only $C_{\mathrm{sat,m}}$ results reported for measurements over a range of temperatures are compared in Figure 5 with those derived in this research (Table 7). Included in Figure 5 are unpublished adiabatic calorimetric measurements made during 1995 at NIPER. The uncertainty for these values is approximately $0.001C_{\mathrm{sat,m}}$. The values of Hough et al.[79] were used by Hatton et al.[54] to define the liquid-phase heat capacities reported in their Table VI. The temperature dependence of those results differs appreciably from that

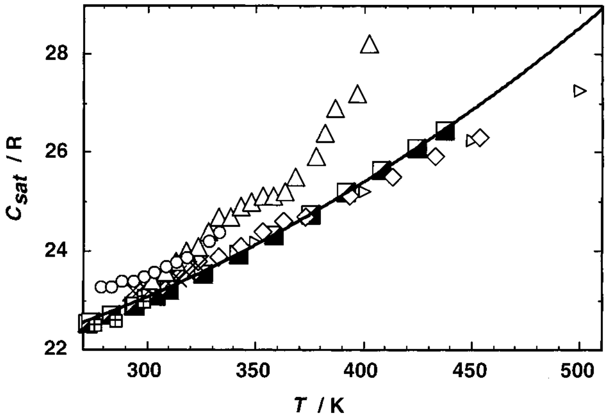

Figure 5. Comparison of literature heat-capacity measurements for benzenamine with those obtained in this research and listed in Table 7. The solid curve represents the results from Table 7. (○) Lang;[85] (△) Blacet et al.;[86] (⊞) Parks et al.;[87] (×) Ferguson and Miller;[88] (◇) Hough et al.;[79] (triangle pointing right) Hatton et al.;[54] (◪) unpublished NIPER measurements by adiabatic calorimetry, 1995.

Table 11. Comparison of Enthalpies of Vaporization Found in a Search of the Literature with Values Derived in This Research

	$\Delta_l^g H_m$	T	Δ^a		$\Delta_l^g H_m$	T	Δ^a
ref	kJ·mol^{-1}	K	kJ·mol^{-1}	ref	kJ·mol^{-1}	K	kJ·mol^{-1}
			Benzenamine				
89	40.6	457.2	−3.3	54	51.28	355.23	−0.05
90	40.9	452	−3.4	54	50.20	370.14	−0.01
54	55.75	298.15	−0.12	54	48.65	392.54	0.07
54^b	52.95	333.12	−0.08	54	47.36	412.03	0.18
54	55.21	304.68	−0.12	54	45.95	434.19	0.37
54	54.39	314.75	−0.11	54	44.53	457.55	0.65
54	53.52	325.72	−0.10	91	55.834	298.15	−0.04
54	52.28	341.74	−0.07				
			Butylbenzene				
113	51.05	298.15	0.20	115	46.02	368	−0.20
114	37.7	456	−2.5	115^c	38.87	456.42	−1.29
115	47.95	343	0.10	115^c	51.36	298.15	0.51
115	46.79	358	−0.08				
			tert-Butylbenzene				
122	47.45	298.15	0.74				

[a] $\Delta = \Delta_l^g H_m(\text{ref}) - \Delta_l^g H_m(\text{this research})$ in units of kJ·mol^{-1}. [b] Experimental measurement (see text). [c] Extrapolated values (see text).

reported here (Table 7). Other data discordant with the results reported in this research include the measurements of Lang[85] and Blacet et al.[86] In contrast, for the results of Parks et al.[87] and Ferguson and Miller,[88] agreement is within the probable uncertainty limits.

Table 11 gives a comparison of enthalpies of vaporization for benzenamine[54,89−91] with values derived in this research (see above and Table 8). All the literature values differ from values obtained in this research by amounts no greater than the estimated overall probable errors in the measurements. Hatton et al.[54] calorimetrically measured enthalpies of vaporization at ~333 K and calculated vapor pressures and enthalpies of vaporization in the temperature range 305 to 458 K using a third-law method. The values of $\Delta = \Delta_l^g H_m(\text{ref}) - \Delta_l^g H_m(\text{this research})$ for the results reported by Hatton et al.[54] increase smoothly with temperature and, therefore, may denote either failure to make any correction for nonideality or application of an incorrect one. Their paper states for $T = 333$ K "the deviation from ideality was checked using the Berthelot equation and found to be negligibly small", which is correct at that pressure (~0.8 kPa). No such statement is made concerning corrections to the enthalpy of vaporization values reported for higher temperatures. For ref 91, which has a measurement obtained with a vaporization calorimeter and not determined via the slope of a vapor-pressure versus temperature plot, Δ is extremely small (<0.1%). This denotes little, if any, error in the extrapolated slope arising from small errors in the Wagner parameters listed in Table 5 for benzenamine.

Butylbenzene. In their review of critical property measurements for aromatics, Tsonopoulos and Ambrose[92] list only three sets of measurements on butylbenzene.[93−95] The literature search within the present project revealed an additional reference: Massart[96] (a paper on density measurements, which includes an equation representing the rectilinear diameter). Ambrose et al.[95] noted that butylbenzene decomposed at the critical point and stated they preferred the earlier results.[94] Tsonopoulos and Ambrose,[92] relying on the comments of Ambrose et al.,[95] recommended the following critical properties: $T_c = (660.5 \pm 0.5)$ K, $p_c = (2890 \pm 40)$ kPa, and $\rho_c = (270 \pm 10)$ kg·m^{-3}. Assuming a critical temperature of 660.5 K, a value of $\rho_c = 279$ kg·m^{-3} is derived from the results reported by Massart.[96] Using the fast-scan technique,[13] results from the DSC for butylbenzene in the critical region were obtained (see Table 3 and Figure 2). A critical temperature of (660.5 ± 1) K was obtained (Table 3 and Figure 2) with a corresponding critical pressure of (2990 ± 200) kPa derived from the fitting procedures. A critical density of (269 ± 9) kg·m^{-3} is recommended (see Table 10).

Figure 6 compares the literature vapor pressures for butylbenzene with values obtained using the Wagner equation and the parameters listed in Table 5. A search of the literature yielded four references listing measured vapor pressures other than VLE end points or other single-point measurements (e.g., boiling points).[97−100] In addition, Ambrose et al.[95] listed parameters to use in conjunction with their eq 3 (their Table 5) for butylbenzene but gave no details of the origin of any measurements to go with that representation. The Ambrose et al.[95] representation agrees excellently with the results reported by Forziati et al.,[98] which in turn are in excellent agreement with those reported in this research. With the exception of two points (369.4 K, 0.27% deviation, and 411.4 K, 0.14% deviation), the results of Forziati et al.[98] agree with those of this research within ±0.05%. In contrast, the results of Linek et al.[99] deviate approximately linearly with temperature from near zero % at 374.4 K to −0.54% at 450 K (see Figure 6B). The low-pressure measurements of Linder[97] and Kasehgari et al.[100] (see Figure 6A) deviate in opposite directions from the extrapolated values derived using the Wagner equation and the parameters listed in Table 5.

Figure 7 compares values for the saturated liquid-phase density of butylbenzene found in the literature search (only those studies which covered a range of at least 10 K)[96,101−109] with values calculated using eq 13 derived from a fit of the measurements reported in Table 4.

$$\rho/\text{kg·m}^{-3} = 268.9 + 589.3(1 - T/660.5)^{1/3} - 70.3(1 - T/660.5)^{2/3} + 274.3(1 - T/660.5) \quad (13)$$

Also included in Figure 7 are representations of the equation for the saturation liquid density for butylbenzene given in the 1985 and 1996 versions of the DIPPR Project 801 Database: the dashed and solid curves, respectively. The DIPPR 801 Project Database representation of the variation of the saturation liquid density of butylbenzene

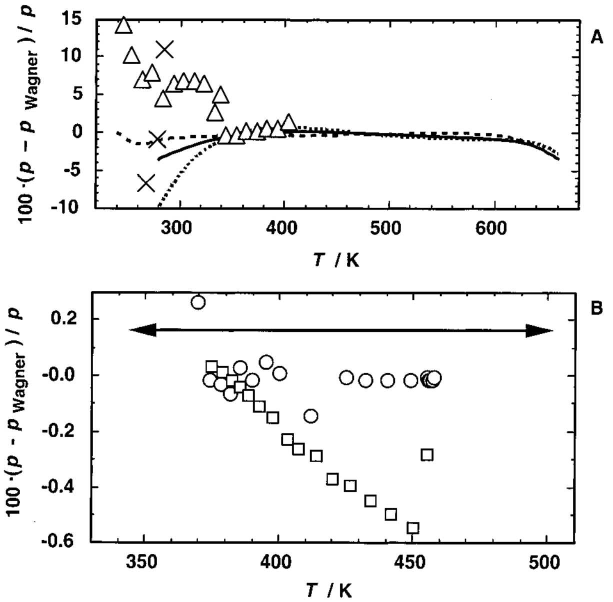

Figure 6. Comparison of literature vapor-pressure measurements for butylbenzene with those obtained using the Wagner equation and the parameters listed in Table 5. (A) (△) Kasehgari et al.;[100] (×) Linder;[97] the dotted curve, the dashed curve, and the solid curve represent the equations for the vapor pressure of butylbenzene given in the DIPPR Project 801 Database 1984 version[36] and the DIPPR Project 801 Database 1995 version[37] and values obtained using the parameters listed in Table 5 of Ambrose et al.[95] in conjunction with their eq 3, respectively. (B) the double arrow denotes the range of the vapor-pressure measurements reported in Table 1; (○) Forziati et al.;[98] (□) Linek et al.[99]

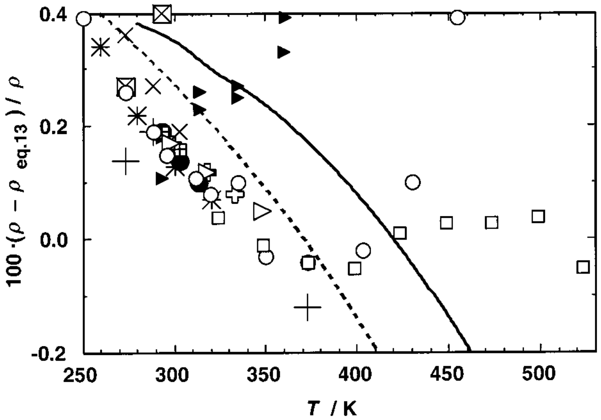

Figure 7. Comparison of literature density measurements for butylbenzene with those obtained using eq 13. The solid and dashed curves represent the equations for the saturation liquid density for butylbenzene given in the 1985 version of the DIPPR Project 801 Database[36] (and the 1996 version,[37] respectively). (□) this research (see Table 4); (+) Balbiano;[101] (× in a box) Konowalow;[102] (×) Timmermans and Martin;[103] (○) Massart;[96] (solid triangle pointing right) Vogel;[104] (⊞) Forziati and Rossini;[105] (●) Donaldson and Quayle;[106] (∗) Barlow et al.;[107] (triangle pointing right) Anderko;[108] (✙) Chyli'nski and Gregorowicz.[109]

with temperature does not reproduce the literature values well. Not shown in Figure 7 are the measurements of Evans[110] in the temperature range 288 K to 373 K and of Buehler et al.[111] in the range 313 K to 374 K, where the average deviations from eq 13 are 1% and 1.4%, respectively.

Liquid-phase heat-capacity $C_{\mathrm{sat,m}}$ values for butylbenzene have been reported in the literature by Huffman et al.[112] and by Messerly et al.[113] Messerly et al. list an equation for the heat capacity of the liquid phase for the temperature range 195 K to 380 K. When compared with the values of $C_{\mathrm{sat,m}}$ listed in Table 7 within the temperature overlap region (300 K to 380 K), the agreement is excellent ($<0.1R$).

Included in Table 11 is a comparison of enthalpies of vaporization for butylbenzene[113−115] with values derived in this research (see above and Table 8). Messerly et al.[113] derived the listed value for 298.15 K using the Clapeyron equation in conjunction with a Cox equation representation of the vapor-pressure measurements of Forziati et al.[98] "Corrections for the effects of gas imperfection were negligible and were omitted." Agreement with the value derived in this research is good, differing by an amount no greater than the estimated overall probable errors in the measurements. The value determined at the normal boiling point by Al-Dharir and Swan,[114] using the gas−liquid chromatographic technique, is too low.

Svoboda et al.[115] measured enthalpies of vaporization at 343 K, 358 K, and 368 K. They note "The error of measurement was estimated on the basis of the accuracy analysis of input data and of respective corrections: it was lower than 0.2%." For the three temperatures, agreement with the results derived in the present research (see Table 11) is within 0.2%, 0.2%, and 0.4%, respectively. Agreement for the extrapolated values at the normal boiling point (456.42 K) and 298.15 K is not nearly as good as that for the measurements and raises questions concerning the extrapolation techniques used by Svoboda et al.[115]

***sec*-Butylbenzene.** No references to previous measurements of the critical properties of *sec*-butylbenzene were found in a literature search through July 1996. Using the fast-scan techniques developed at NIPER (see ref 13), a critical temperature $T_c = (652.5 \pm 1)$ K was obtained (Table 3 and Figure 2C) with a corresponding critical pressure of (3025 ± 200) kPa derived from the fitting procedures. A critical density of $(274 \pm 9)\ \mathrm{kg{\cdot}m^{-3}}$ is recommended (see Table 10).

Figure 8 compares literature results for the vapor pressure of *sec*-butylbenzene with values obtained using the Wagner equation and the parameters listed in Table 5. The literature search gave three references listing measured vapor pressures other than VLE end points or other single-point measurements (e.g., boiling points).[97,98,100] With the exception of one point (360.2 K, 0.5% deviation), the Forziati et al.[98] results agree with those of this research within ±0.1% (see Figure 8B). In contrast, within the region where there is overlap with the measurements made in this research, the results of Kasehgari et al.[100] have a positive bias averaging 0.6% (see Figure 8A). For the low-pressure measurements of Linder,[97] deviations range from −47% at 264.6 K to −21% at 283.8 K. The measurements of Linder[97] and Kasehgari et al.[100] deviate in opposite directions from the extrapolated values derived using the Wagner equation and the parameters listed in Table 5. The DIPPR 801 Project Database representation follows the trend of the Linder measurements.

Figure 9 compares values for the saturated liquid-phase density of *sec*-butylbenzene found in the literature search (only those studies which covered a range of at least 10 K)[105−107,116,117] with values calculated using eq 14 derived from a fit of the measurements reported in Table 4.

$$\rho/\mathrm{kg{\cdot}m^{-3}} = 273.7 + 573.0(1 - T/652.5)^{1/3} - 9.56(1 - T/652.5)^{2/3} + 224.0(1 - T/652.5) \quad (14)$$

Values measured by Estreicher[116] are in excellent agreement (±0.1%) with those obtained by extrapolation of eq 14.

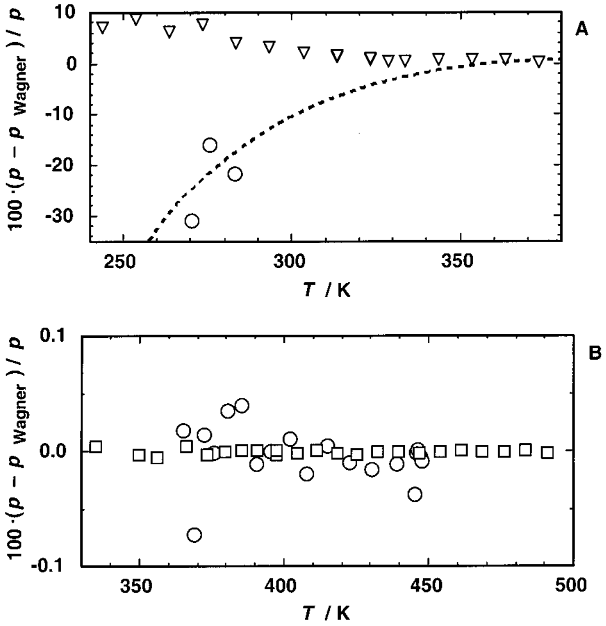

Figure 8. Comparison of literature vapor-pressure measurements for *sec*-butylbenzene with those obtained using the Wagner equation and the parameters listed in Table 5. (A) The dashed line represents the vapor-pressure equation of the DIPPR Project 801 Database;[37] (▽) Kasehgari et al.;[100] (○) Linder,[97] only three of the four points shown (see text). (B) (□) this research (Table 1); (○) Forziati et al.[98]

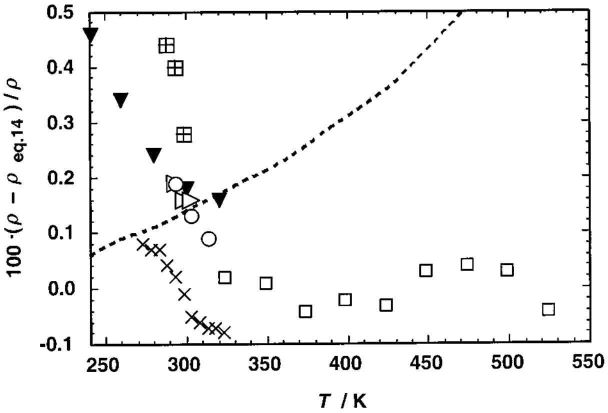

Figure 9. Comparison of literature density measurements for *sec*-butylbenzene with those obtained using eq 14. The dashed line represents the saturation densities derived using the equation of the DIPPR Project 801 Database;[37] (□) this research (see Table 4); (×) Estreicher;[116] (⊞) Harrison et al.;[117] (triangle pointing right) Forziati and Rossini;[105] (○) Donaldson and Quayle;[106] (▼) Barlow et al.[107]

Liquid-phase heat-capacity $C_{\mathrm{sat,m}}$ values for *sec*-butylbenzene were reported in the literature by Andolenko and Grigorév.[118] When compared with the values of $C_{\mathrm{sat,m}}$ listed in Table 7, the agreement is excellent ($\pm 0.1R$ across the whole temperature range, 294 K to 430 K, listed by Andolenko and Grigorév).

***tert*-Butylbenzene.** Tsonopoulos and Ambrose[92] list no references to previous measurements of the critical properties of *tert*-butylbenzene. The literature search found one reference[119] with measurements of the critical temperature and pressure with derivation of the critical density using the law of rectilinear diameters: $T_c = (648.31 \pm 0.51)$ K, $p_c = (2979 \pm 20)$ kPa, and $\rho_c = (284.6 \pm 2.1)$ kg·m^{-3}. Using the fast-scan techniques of this research, a critical temperature $T_c = (647.5 \pm 1)$ K was obtained with a corresponding critical pressure of (2900 ± 200) kPa derived from the fitting procedures. A critical density of (277 ± 9) kg·m^{-3} is recommended (see Table 10).

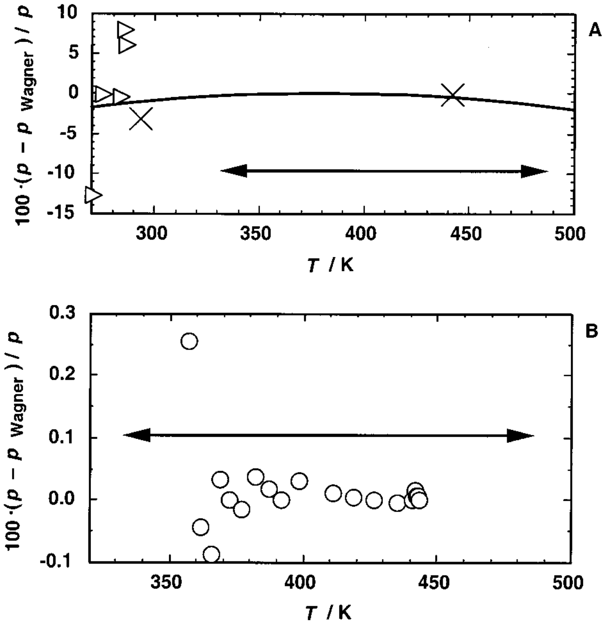

Figure 10. Comparison of literature vapor-pressure measurements for *tert*-butylbenzene with those obtained using the Wagner equation and the parameters listed in Table 5. The double-headed arrow represents the range of the measurements made in the present research (Table 1). (A) The solid line represents the vapor-pressure equation of the DIPPR Project 801 Database;[37] (triangle pointing right) Linder;[97] (×) Dubinin et al.[120] (B) (○) Forziati et al.[98]

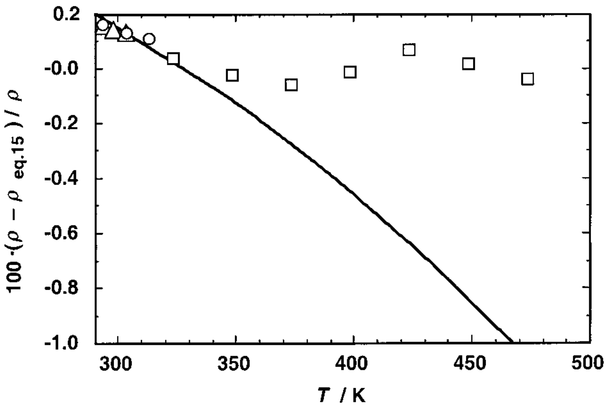

Figure 11. Comparison of literature density measurements for *tert*-butylbenzene with those obtained using eq 15. The solid line represents the saturation densities derived using the equation of the DIPPR Project 801 Database;[37] (□) this research (see Table 4); (△) Forziati and Rossini;[105] (○) Donaldson and Quayle.[106]

Figure 10 compares literature results for the vapor pressure of *tert*-butylbenzene with values obtained using the Wagner equation and the parameters listed in Table 5. The literature search gave three references listing measured vapor pressures other than VLE end points or other single-point measurements.[97,98,120] With the exception of one point (357 K, 0.26% deviation), the Forziati et al.[98] results agree with those of this research within ±0.1% (see Figure 10B). As for the other butylbenzene isomers of the study, the measurements of Linder[97] show large deviations from the extrapolated values derived using the Wagner equation and the parameters listed in Table 5.

Figure 11 compares values for the saturated liquid-phase density of *tert*-butylbenzene found in the literature search (only those studies which covered a range of at least 10

K)[105,106] with values calculated using eq 15 derived from a fit of the measurements reported in Table 4.

$$\rho/\text{kg}\cdot\text{m}^{-3} = 277.1 + 641.7(1 - T/647.5)^{1/3} - 187.8(1 - T/647.5)^{2/3} + 334.9(1 - T/647.5) \quad (15)$$

Liquid-phase heat-capacity $C_{\text{sat,m}}$ values for *tert*-butylbenzene have been reported in the literature by Huffman et al.[121] for the temperature region from the triple point to 294 K. When compared with extrapolated values of $C_{\text{sat,m}}$ (obtained using the values listed in Table 7 fitted to a cubic equation in temperature), the agreement is good (within 0.2*R*).

Included in Table 11 is an enthalpy of vaporization measurement at 298.15 K for *tert*-butylbenzene by Peacock and Fuchs.[122] The measurement was derived using a gas chromatographic technique. Agreement with the value derived in this research is good, differing by an amount no greater than the estimated overall probable errors in the measurements.

2,2-Dimethylbutanoic Acid. A critical temperature of (655 ± 15) K, a corresponding critical pressure of (3850 ± 500) kPa, and a critical density of (272 ± 15) kg·m^{-3} were obtained from the fitting procedures used in this research for 2,2-dimethylbutanoic acid. No literature references to measurements of critical properties were found. The only reference to any properties found, which contained other than a single datum measurement, was due to Hommelen,[123] who listed two density and boiling point values for the acid. The values for the density, 944.9 kg·m^{-3} at 273 K and 927.6 kg·m^{-3} at 293 K, compare with the values 942.9 kg·m^{-3} and 925.6 kg·m^{-3}, respectively, obtained by extrapolation of the results of this research, which are represented by eq 16.

$$\rho/\text{kg}\cdot\text{m}^{-3} = 272.4 + 1055.3(1 - T/655)^{1/3} - 1062.1(1 - T/655)^{2/3} + 909.4(1 - T/655) \quad (16)$$

Hommelen[123] lists a vapor pressure of 2.67 kPa at 369 K and a temperature range of 377 to 378 K for a pressure of 4.27 kPa. Using the Wagner equation and the parameters listed in Table 5, a pressure of 2.65 kPa is derived for 369 K, and over the temperature range 377 to 378 K, pressures correspond to 4 kPa to 4.2 kPa, all in good agreement with Hommelen's values. Figure 12 compares the Hommelen values and the DIPPR Project 801 Database[37] vapor-pressure equation with the values obtained in this research (Table 1).

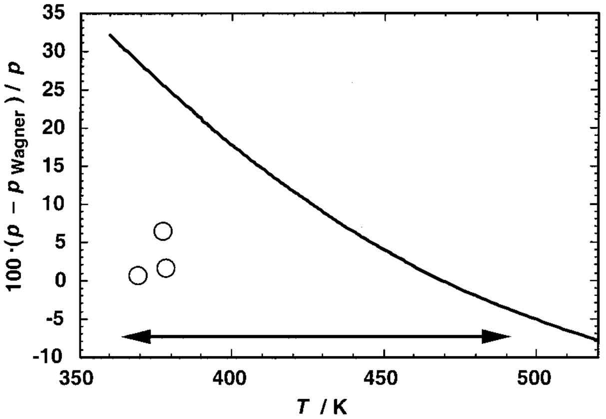

Figure 12. Comparison of literature vapor-pressure measurements for 2,2-dimethylbutanoic acid with those obtained using the Wagner equation and the parameters listed in Table 5. The double-headed arrow represents the range of measurements made in the present research (Table 1). The solid line represents the vapor-pressure equation of the DIPPR Project 801 Database;[37] (○) Hommelen.[123]

Tridecafluoroheptanoic Acid. A critical temperature of (583 ± 15) K, a corresponding critical pressure of (2075 ± 500) kPa, and a critical density of (509 ± 15) kg·m^{-3} were used in this research for corresponding-states estimations for tridecafluoroheptanoic acid (Table 10). No literature references to measurements of the critical properties were located. Several references were found in the literature search that contained data for the fluoroacid. Kauck and Diesslin[124] listed a density of 1792 kg·m^{-3} at 293 K with a boiling point of 448 K at 98.9 kPa pressure. A density of 1790 kg·m^{-3} at 293 K is obtained by extrapolation of the results of this research, which are represented by eq 17.

$$\rho/\text{kg}\cdot\text{m}^{-3} = 508.8 + 1580.8(1 - T/583)^{1/3} - 662.7(1 - T/583)^{2/3} + 894.7(1 - T/583) \quad (17)$$

Interpolation of the Wagner equation with the parameters listed in Table 5 gives a vapor pressure of 95.5 kPa at 448 K for tridecafluoroheptanoic acid. Huang et al.[125] listed a melting range of 304−309 K (recrystallized from carbon tetrachloride) and normal boiling range of 448−450 K for their sample prepared while developing a new synthesis method for fluoroacids. A melting point of 308.7 K was obtained during the DSC measurements (see Table 2), and the normal boiling point interpolated using the Wagner equation with the parameters listed in Table 5 is 450.03 K. In contrast, Benefice-Malouet et al.[126] listed a melting point of 327 K (also recrystallized from carbon tetrachloride) and a boiling point of 378 K at 5.33 kPa (interpolation gives 5.69 kPa at that temperature).

2-Butyl-2-ethyl-1,3-propanediol. Because of extensive decomposition at 523 K, no critical properties could be determined for this diol. Few thermophysical property measurements were located in the literature search. The Union Carbide text "Glycols"[127] lists a melting point of 314.6 K and a boiling point of 468 K at 13.3 kPa with a corresponding apparent specific gravity 50/20 °C value of 0.931. The DSC measurement gave a melting point of 317.3 K for the purified samples used in this research. A value of 12.7 kPa is interpolated for the pressure at 468 K. The specific gravity reading is translated to mean a density of 929 kg·m^{-3} at 323 K, which can be compared with a value of 926.8 kg·m^{-3} at 323.149 K listed in Table 4. Four other references listed melting points and reduced-pressure boiling points for 2-butyl-2-ethyl-1,3-propanediol.[128−131] Only the results of Weilbull and Matell[131] are in the same range as those obtained in this research [melting point 313−316 K, boiling point 409−416 K at 1.067 kPa (cf., 411 K for 1.067 kPa)].

2,2,4-Trimethyl-1,3-pentanediol. Because of extensive decomposition at above 496 K, no critical properties could be determined for this diol. The DIPPR Project 801 Database[37] lists the full range of properties for 2,2,4-trimethyl-1,3-pentanediol, most of which are estimates derived using various correlation techniques. Literature values abstracted by the 801 Project were the same as those obtained in the present literature search. No additional references were located.

Comparison of literature vapor-pressure measurements[132−137] (reduced pressure boiling points) for 2,2,4-trimethyl-1,3-pentanediol with those obtained using the Antoine equation and the parameters listed in Table 6 is made in Figure 13. In the figure the double-headed arrow represents the range of the measurements made in the

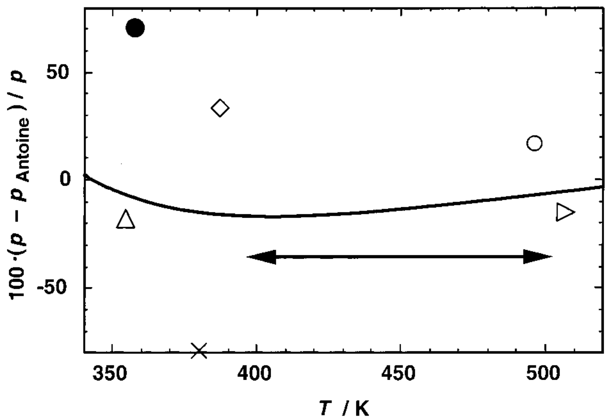

Figure 13. Comparison of literature vapor-pressure measurements for 2,2,4-trimethyl-1,3-pentanediol with those obtained using the Antoine equation and the parameters listed in Table 6. The double-headed arrow represents the range of measurements made in the present research (Table 1B). The solid line represents the vapor-pressure equation of the DIPPR Project 801 Database;[37] (○) Fossek;[132] (triangle pointing right) Grignard and Iliesco;[133] (△) Kulpinski and Nord;[134] (●) Greene et al.;[135] (◇) Baltz et al.;[136] (×) Gavrilova et al.[137]

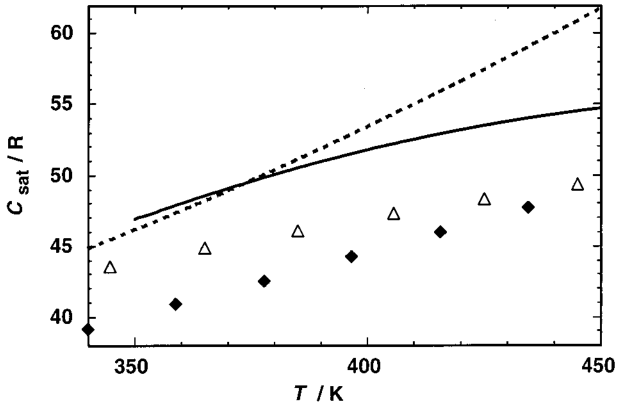

Figure 14. Comparison of heat capacities along the saturation line, C_{sat}, for 2,2,4-trimethyl-1,3-pentanediol with those obtained with DSC and reported in Table 2. The solid line represents the measurements of this research (Table 2); the dashed line represents the correlation of Ruzicka and Domalski;[138] (◆) the Chueh and Swanson correlation;[139] (△) the Lee Kesler correlation.[140]

present research (Table 1B) and the solid line represents the vapor-pressure equation of the DIPPR Project 801 Database.[37] Considering the small amount of available measurements, the DIPPR 801 vapor-pressure equation is a good estimate. The liquid-phase density along the saturation line correlation is poor, ranging from 6 to 7.5% low relative to the measurements listed in Table 4.

Figure 14 compares the measured heat capacities C_{sat} for 2,2,4-trimethyl-1,3-pentanediol with values derived by the methods of Ruzicka and Domalski,[138] Chueh and Swanson,[139] and the Lee Kesler[140] correlation. None of the correlations reproduce the experimental measurements. Only the Lee Kesler correlation reproduces the temperature dependence of the measurements, which is characteristic of hydrogen-bonded compounds.[26] For the other diol, 2-butyl-2-ethyl-1,3-propanediol, the Ruzicka and Domalski[138] correlation shows a similar failure to reproduce the temperature dependence for that hydrogen-bonded compound.

1-Chloro-2-propanol. For this compound, extensive decomposition above 405 K prevented critical property measurements. The literature search gave a reference to vapor-pressure measurements for 1-chloro-2-propanol performed by Kireev and Nikiforova.[141] Figure 15 compares the measurements of Kireev and Nikiforova with values obtained using the Antoine equation and the parameters listed in Table 6. Other than the Russian reference, only single-point density measurements and reduced-pressure boiling points were located.

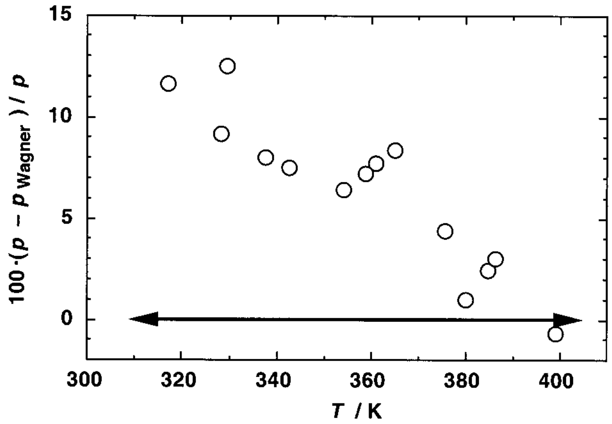

Figure 15. Comparison of literature vapor-pressure measurements for 1-chloro-2-propanol with those obtained using the Antoine equation and the parameters listed in Table 6. The double-headed arrow represents the range of the measurements made in the present research (Table 1B). (○) Kireev and Nikiforova.[141]

Acknowledgment

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