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Vapor Pressure, Heat Capacity, and Density along the Saturation Line, Measurements for Cyclohexanol, 2-Cyclohexen-1-one, 1,2-Dichloropropane, 1,4-Di-*tert*-butylbenzene, (±)-2-Ethylhexanoic Acid, 2-(Methylamino)ethanol, Perfluoro-*n*-heptane, and Sulfolane

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This paper reports measurements made for DIPPR Research Project 821 in the 1994 Project Year. Vapor pressures were measured to a pressure limit of 270 kPa or lower decomposition point for eight compounds using a twin ebulliometric apparatus. Liquid-phase densities along the saturation line were measured for each compound over a range of temperatures (ambient to a maximum of 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 [within the temperature range (±50 K) of the vapor pressures], enthalpies of fusion if solid at ambient temperature, solubility parameter, and heat capacities along the saturation line. Wagner-type vapor-pressure equations were derived for each compound. In addition, the liquid-phase densities were compared with values derived using a four-term power series in either T or $[(1 - T_r)^{1/3}]$. 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 was used to estimate thermal decomposition temperatures by radical scission from a knowledge of the bond dissociation energy or vice versa.

Introduction

The previous paper (Steele et al., 1997) details the background, equipment used etc., in measurements made within the DIPPR 821 Vapor Pressures of Industrial Interest Research Program at Bartlesville, OK. 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 differential scanning calorimetry (DSC) method developed at the National Institute for Petroleum & Energy Research (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 (Wagner, 1973); 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 solubility parameter for each compound.

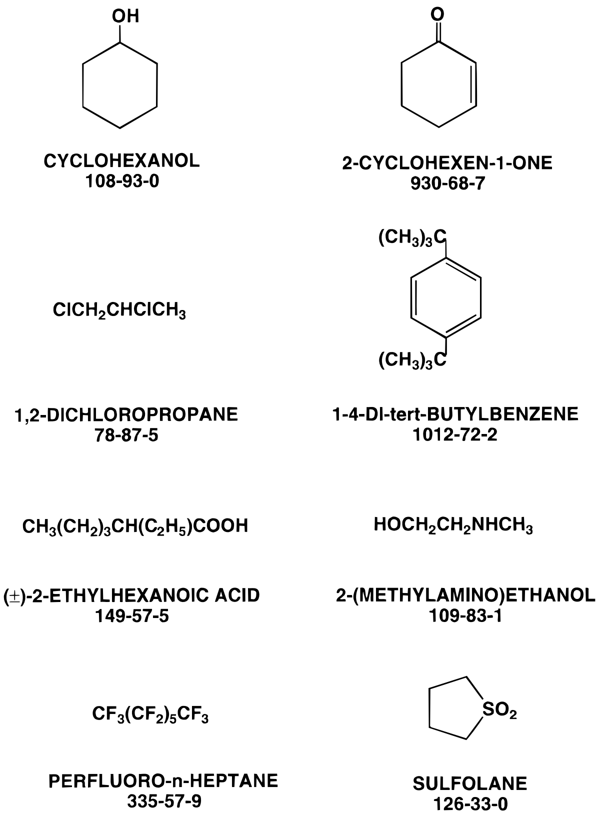

Figure 1. Structural formulas, common names, and Chemical Abstract Services Registry Numbers (provided by the authors) for the compounds studied in this research.

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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
Perfluoro-*n*-heptane											
d	341.241	1.9888	0.0030	0.0002	0.032	w	410.399	47.362	0.010	0.003	0.010
d	353.664	4.0064	0.0010	0.0003	0.025	w	416.205	57.807	0.009	0.003	0.009
d	359.071	5.3218	−0.0004	0.0004	0.021	w	422.063	70.112	0.004	0.004	0.009
d	367.248	7.9982	−0.0014	0.0005	0.022	w	427.975	84.528	−0.003	0.004	0.010
d	373.350	10.6651	−0.0013	0.0006	0.019	w	433.942	101.317	−0.016	0.005	0.010
d	378.249	13.310	−0.001	0.001	0.016	w	439.964	120.78	−0.02	0.01	0.011
d	383.427	16.673	−0.001	0.001	0.013	w	446.053	143.24	−0.03	0.01	0.010
d	387.683	19.937	0.000	0.001	0.012	w	452.195	169.01	−0.01	0.01	0.011
w	393.321	25.050	0.002	0.001	0.012	w	458.402	198.50	0.05	0.01	0.013
w	398.980	31.209	0.003	0.002	0.010	w	464.662[b]	232.00	0.17	0.01	0.014
w	404.657	38.563	0.004	0.002	0.010	w	470.984[b]	269.98	0.38	0.01	0.017
2-Cylohexen-1-one											
d	334.844	1.9986	0.0002	0.0001	0.039	w	417.568	47.380	−0.002	0.002	0.007
d	356.065	5.3256	−0.0011	0.0003	0.014	w	424.468	57.802	−0.001	0.003	0.009
d	365.845	7.9982	0.0001	0.0005	0.010	w	431.433	70.109	−0.004	0.003	0.006
d	373.175	10.6687	0.0005	0.0006	0.007	w	438.439	84.520	−0.006	0.004	0.006
d	379.065	13.319	0.000	0.001	0.004	w	445.489	101.311	−0.003	0.004	0.007
d	385.244	16.664	0.001	0.001	0.005	w	452.590	120.80	0.01	0.01	0.009
d	390.360	19.933	0.000	0.001	0.005	w	459.723[b]	143.27	0.06	0.01	0.015
d	397.086	25.018	0.001	0.001	0.006	w	466.889[b]	169.00	0.11	0.01	0.018
w	403.875	31.181	0.001	0.002	0.006	w	474.117[b]	198.53	0.21	0.01	0.026
w	410.687	38.556	0.000	0.002	0.006	w	481.361[b]	232.07	0.41	0.01	0.049
1,2-Dichloropropane											
d	293.673	5.3334	0.0001	0.0004	0.014	w	351.511	57.802	−0.003	0.003	0.008
d	301.838	7.9820	0.0001	0.0005	0.012	w	357.437	70.109	−0.003	0.004	0.009
d	308.039	10.6580	−0.0004	0.0006	0.012	w	363.413	84.541	0.001	0.004	0.009
d	313.031	13.319	−0.001	0.001	0.011	w	369.425	101.326	0.002	0.005	0.009
d	318.274	16.681	0.000	0.001	0.011	w	375.489	120.81	0.01	0.01	0.010
d	322.569	19.929	0.001	0.001	0.009	w	381.593	143.25	0.00	0.01	0.009
d	328.301	25.051	0.002	0.001	0.010	w	387.751	169.05	0.00	0.01	0.010
w	334.048	31.212	−0.001	0.002	0.009	w	393.945	198.50	−0.01	0.01	0.011
w	339.810	38.571	0.000	0.002	0.010	w	400.186	232.03	0.00	0.01	0.013
w	345.633	47.363	−0.002	0.003	0.009	w	406.461	269.98	0.01	0.01	0.017
1,4-Di-*tert*-butylbenzene											
d	387.021	1.9964	−0.0001	0.0001	0.016	w	479.129	47.362	−0.001	0.002	−0.001
d	403.301	3.9924	0.0000	0.0002	0.007	w	486.883	57.825	−0.001	0.003	−0.001
d	410.690	5.3462	0.0001	0.0003	0.004	w	494.675	70.123	0.000	0.003	0.000
d	421.455	7.9956	0.0003	0.0004	0.002	w	502.525	84.529	0.001	0.004	−0.002
d	429.612	10.6660	0.0000	0.0006	0.002	w	510.433	101.312	−0.001	0.004	−0.001
d	436.206	13.333	0.000	0.001	0.000	w	518.399	120.77	0.00	0.01	0.000
d	443.093	16.683	0.000	0.001	0.000	w	526.425	143.22	0.00	0.01	0.002
d	448.750	19.928	−0.001	0.001	−0.001	w	534.507	169.01	0.00	0.01	0.001
d	456.253	25.012	0.000	0.001	−0.001	w	542.640	198.46	0.01	0.01	0.002
w	456.314[c]	25.058	0.001	0.001	−0.002	w	550.823	231.96	0.00	0.01	0.001
w	463.830	31.173	0.000	0.002	−0.002	w	559.061	269.96	−0.01	0.01	0.004
w	471.457	38.565	0.001	0.002	0.000						
(±)-2-Ethylhexanoic Acid											
d	397.184	1.9992	−0.0001	0.0001	0.043	w	462.322	31.157	−0.003	0.002	0.012
d	411.316	4.0042	0.0001	0.0003	0.025	w	468.678	38.596	0.000	0.002	0.013
d	417.544	5.3338	0.0002	0.0003	0.019	w	474.989	47.368	0.001	0.002	0.016
d	426.783	7.9981	0.0006	0.0005	0.013	w	481.354	57.799	0.001	0.003	0.018
d	433.676	10.6602	0.0000	0.0006	0.010	w	487.756	70.106	0.006	0.003	0.025
d	439.290	13.353	0.000	0.001	0.010	w	494.190	84.521	0.008	0.004	0.035
d	444.993	16.654	0.000	0.001	0.008	w	500.662	101.326	0.006	0.005	0.050
d	449.764	19.919	−0.001	0.001	0.008	w	507.167[b]	120.78	−0.02	0.01	0.065
d	456.062	25.034	−0.002	0.001	0.010	w	513.691[b]	143.24	0.03	0.01	0.097
w	456.048[c]	25.021	−0.002	0.001	0.011						
2-(Methylamino)ethanol											
d	340.269	2.0042	−0.0004	0.0002	0.063	w	404.193	38.559	0.012	0.002	0.023
d	352.927[d]	3.9996	0.0055	0.0003	0.047	w	409.810	47.380	0.012	0.003	0.024
d	358.594	5.3384	0.0012	0.0004	0.049	w	415.427	57.812	0.012	0.003	0.025
d	366.878	7.9994	0.0027	0.0005	0.040	w	421.068	70.118	0.005	0.004	0.026
d	373.059	10.6628	0.0022	0.0006	0.036	w	426.719	84.528	0.004	0.004	0.027
d	378.057	13.339	0.001	0.001	0.032	w	432.388	101.318	−0.004	0.005	0.028
d	383.222	16.684	−0.004	0.001	0.029	w	438.070	120.77	0.00	0.01	0.030
d	387.461	19.937	−0.009	0.001	0.025	w	443.781	143.25	−0.01	0.01	0.029
d	393.041	25.021	−0.022	0.001	0.018	w	449.498	169.00	0.00	0.01	0.033
w	393.016[c]	25.032	0.015	0.002	0.018	w	455.246	198.48	0.00	0.01	0.035
w	398.595	31.171	0.010	0.002	0.022	w	461.003	231.97	0.00	0.01	0.036
Perfluoro-*n*-heptane											
d	303.677	13.335	0.000	0.001	0.005	w	317.675[c]	25.019	0.001	0.002	0.004
d	308.468	16.674	0.000	0.001	0.005	w	322.988	31.204	0.001	0.002	0.004
d	312.428	19.927	0.000	0.001	0.004	w	328.292	38.557	0.001	0.002	0.004
d	317.683	25.027	0.000	0.001	0.004	w	333.676	47.385	0.000	0.003	0.004

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
					Perfluoro-*n*-heptane						
w	339.073	57.789	−0.001	0.003	0.004	w	366.806	143.25	0.00	0.01	0.004
w	344.553	70.139	−0.002	0.004	0.004	w	372.475	169.03	0.00	0.01	0.004
w	350.037	84.504	−0.002	0.004	0.004	w	378.184	198.49	0.00	0.01	0.005
w	355.586	101.309	0.000	0.005	0.004	w	383.928	232.01	0.00	0.01	0.005
w	361.174	120.78	0.00	0.01	0.004	w	389.712	270.01	−0.01	0.01	0.005
					Sulfolane						
d	423.822	2.0003	−0.0002	0.0001	0.072	d	500.292	25.020	0.000	0.001	0.010
d	441.881	3.9927	0.0004	0.0002	0.044	w	500.295[c]	25.026	0.004	0.001	0.010
d	449.994	5.3307	0.0005	0.0003	0.029	w	508.562	31.177	0.005	0.002	0.010
d	462.039	8.0065	0.0001	0.0004	0.027	w	516.893	38.586	0.007	0.002	0.008
d	470.981	10.6579	−0.0002	0.0005	0.018	w	525.223	47.369	−0.001	0.002	0.012
d	478.246	13.320	−0.001	0.001	0.014	w	533.620	57.817	−0.006	0.003	0.027
d	485.803	16.660	−0.001	0.001	0.012	w	542.058[b]	70.128	−0.021	0.003	0.040
d	492.058	19.926	−0.001	0.001	0.011						

[a] Water (w) or *n*-decane (d) refers to which material was used in the reference ebulliometer. T is the condensation temperature of the sample. The pressure p was calculated from the condensation temperature of the reference substance. Δp is the difference of the value of pressure, calculated with eq 2 and the parameters listed in Table 5, from the observed value of pressure ($\Delta p = p - p_{\mathrm{Wagner}}$). σ is the propagated error calculated using $\sigma(p) = (0.001)\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\}^{1/2}$ (ebulliometer). ΔT is the difference between the boiling and condensation temperatures ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the sample. [b] Values at this temperature were not included in the fit of the Wagner equation because sample decomposition was indicated by the increase in the ΔT values. [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 pressure measurement standards. [d] 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.

Figure 1 lists the structural formulas, names, and Chemical Abstracts Service registry numbers (CAS No.) for each of the compounds studied in the 1994 Project Year for DIPPR Project 821.

Experimental Section

The apparatus and procedures used in obtaining the experimental data have been previously described in the literature and in various DOE reports. In addition, the earlier papers published in this Journal under the DIPPR auspices (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 except the perfluoro-*n*-heptane, which was a 99.97 mol % pure sample obtained in the early 1950s for calorimetric measurements and kept at Bartlesville sealed under vacuum in glass in “cold storage”. 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.

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). 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 cyclohexanol, 2-cyclohexen-1-one, 1,2-dichloropropane, 1,4-di-*tert*-butylbenzene, (±)-2-ethylhexanoic acid, 2-(2-methylamino)ethanol, perfluoro-*n*-heptane, and sulfolane are listed in Table 1. The vapor pressures, the condensation temperatures, and the difference between the condensation and boiling temperatures for the samples are reported. The small differences between the boiling and condensation temperatures in the ebulliometric measurements indicated correct operation of the equipment and the high purity of the samples studied. In Table 1 significant increases in the difference between the boiling and condensation temperatures are specially noted. This phenomenon normally indicates sample decomposition. Onset of sample decomposition was probable for cyclohexanol above 464 K, for 2-cyclohexen-1-one above 459 K, for (±)-2-ethylhexanoic acid above 507 K, and for sulfolane above 542 K.

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

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
Cyclohexanol							
mass/g	0.008 462	0.014 555	0.021 728	vol cell/(cm^3)	0.052 2	0.052 2	0.052 2
310.0	27.1	27.2	27.2	470.0	40.4	39.0	38.5
330.1	29.9	30.0	30.0	490.0	41.4	39.3	38.7
350.0	32.5	32.6	32.7	510.1	42.4	39.9	39.1
370.0	34.8	34.7	34.7	530.0	43.5	40.6	39.3
390.1	36.3	36.2	36.2	550.0	45.3	41.5	39.7
410.0	37.5	37.4	37.0	570.1	46.4	41.7	40.7
430.0	38.5	38.2	37.7	590.0	49.2	43.3	41.3
450.1	39.3	38.4	38.1				
2-Cyclohexen-1-one							
mass/g	0.008 306	0.014 093	0.021 810	vol cell/(cm^3)	0.052 2	0.052 2	0.052 2
310.0	20.7	20.8	20.9	430.0	26.7	26.2	26.0
330.1	21.3	21.5	21.7	450.1	28.0	27.2	26.9
350.0	22.0	22.5	22.6	470.0	29.2	28.3	27.8
370.0	23.3	23.3	23.4	490.0	30.6	29.4	28.9
390.1	24.1	24.3	24.4	510.1	32.5	30.8	29.8
410.0	25.2	25.3	25.1	530.0	34.0	33.1	31.3
1,2-Dichloropropane							
mass/g	0.009 688	0.015 864	0.022 664	vol cell/(cm^3)	0.052 2	0.052 2	0.052 2
310.0	19.4	19.1	19.2	430.0	25.8	23.6	22.9
330.1	20.1	19.3	19.8	450.1	26.7	24.6	23.8
350.0	21.1	20.0	20.2	470.0	27.1	25.2	24.7
370.0	21.8	20.9	20.9	490.0	30.1	38.1	25.2
390.1	23.1	21.9	21.4	510.1			26.4
410.0	24.4	23.0	22.1				
1,4-Di-*tert*-butylbenzene							
mass/g	0.010 898	0.016 698	0.026 825	vol cell/(cm^3)	0.052 2	0.052 2	0.052 2
Crystals							
300.0	39.1	39.0	39.2	320.0	42.1	42.0	41.9
310.0	40.5	40.5	40.6	330.0	43.4	43.4	43.5
Liquid							
370.0	48.6	48.5	48.8	510.1	62.3	62.1	60.6
390.1	50.6	50.6	50.6	530.0	64.4	63.8	62.0
410.0	52.5	52.4	52.4	550.0	66.5	65.2	63.7
430.0	54.2	54.5	54.3	570.1	68.5	66.9	65.4
450.1	56.6	56.4	55.8	590.0	70.7	68.5	66.6
470.0	58.6	58.4	57.6	610.0	72.7	70.4	68.3
490.0	60.2	60.0	59.1				

crystalline $C_{\mathrm{sat,m}}/R = 0.145T - 4.40$ (in temperature range 290 to 350.8 K)

liquid $C_{\mathrm{sat,m}}/R = 0.089T + 15.92$ (in temperature range 350.8 to 420 K)

$\Delta^{\mathrm{l}}_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(341.5\ \mathrm{K}) = (22.48 \pm 0.4)$ kJmol^{-1} $\Delta^{\mathrm{l}}_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K}) = (21.5 \pm 0.6)$ kJmol^{-1}

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
(±)-2-Ethylhexanoic Acid							
mass/g	0.007 702	0.015 635	0.019 980	vol cell/(cm^3)	0.052 2	0.052 2	0.052 2
310.0	35.8	36.4	36.1	430.0	48.7	46.8	47.0
330.1	38.5	37.8	37.7	450.1	50.9	48.5	48.8
350.0	40.3	39.4	39.4	470.0	53.4	50.8	50.5
370.0	42.4	41.5	41.1	490.0	56.5	52.7	52.4
390.1	44.2	43.3	42.9	510.1	62.5	54.8	53.9
410.0	46.2	45.2	44.9				
2-(Methylamino)ethanol							
mass/g	0.009 241	0.014 559	0.019 551	vol cell/(cm^3)	0.052 2	0.052 2	0.052 2
310.0	24.6	23.7	23.9	450.0	33.5	32.3	31.9
330.1	25.4	24.8	24.7	470.1	35.2	33.5	32.9
350.1	26.2	25.7	25.7	490.0	36.8	34.6	34.0
370.0	27.4	26.8	27.1	510.0	38.4	35.6	34.8
390.0	28.5	28.2	28.0	530.1	40.4	37.0	35.8
410.1	30.4	29.5	29.5	550.0	41.4	38.3	36.3
430.0	31.8	30.9	30.6				
Perfluoro-*n*-heptane							
mass/g	0.017 312	0.024 295	0.038 114	vol cell/(cm^3)	0.052 2	0.052 2	0.052 2
310.0	52.2	52.1	51.3	410.0	66.2	62.4	59.5
330.0	54.3	53.7	52.8	430.0	70.2	65.3	61.7
350.0	56.9	55.6	54.4	450.0	76.3	70.2	64.5
370.0	59.8	57.7	56.1	470.0^b	66.4	71.8	65.9
390.0	62.8	60.1	57.8				

Table 2 (Continued)

T/K	$C^{II}_{x,m}$/R	$C^{II}_{x,m}$/R	$C^{II}_{x,m}$/R	T/K	$C^{II}_{x,m}$/R	$C^{II}_{x,m}$/R	$C^{II}_{x,m}$/R
			Sulfolane				
mass/g	0.012 420	0.017 246	0.024 969	vol cell/(cm^3)	0.052 2	0.052 2	0.052 2
315.1	22.2	22.2	22.2	455.0	27.5	27.5	27.5
335.0	23.0	22.9	23.0	475.0	27.8	28.1	28.2
355.0	23.8	23.5	23.6	495.1	28.5	28.8	28.8
375.1	24.2	24.3	24.4	515.0	29.1	29.5	29.5
395.0	25.1	25.3	25.1	535.0	30.4	30.0	30.3
415.0	25.9	26.0	26.1	555.1[b]	31.3	30.9	30.8
435.1	26.5	26.7	26.3				

[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.

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

ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})	T/K
Cyclohexanol		Dichloropropane	
159.4	636.0	237.0	569.6
212.5	643.9	312.0	576.1
274.1	647.0	440.2	577.5
341.7	646.1		
409.4	640.0		
1,4-Di-*tert*-butylbenzene		Perfluoro-*n*-heptane	
78.9	671.2	199.5	464.0
204.4	703.8	278.2	468.1
254.4	706.0	329.4	469.6
313.0	707.0	462.1	473.5
351.6	700.3	566.8	474.6
504.9	656.0	725.3	472.6

For 2-cyclohexen-1-one, (±)-2-ethylhexanoic acid, 2-(methylamino)ethanol, and sulfolane, extensive sample decomposition precluded attainment of heat-capacity measurements above the highest listed temperatures. For cyclohexanol, 1,2-dichloropropane, 1,4-di-*tert*-butylbenzene, and perfluoro-*n*-heptane, measurements in the critical region were possible. For those latter 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 the equation

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

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

Critical temperatures and critical densities were derived graphically for cyclohexanol, 1,2-dichloropropane, 1,4-di-*tert*-butylbenzene, and perfluoro-*n*-heptane, 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., 1991a), dibenzothiophene (Chirico et al., 1991), and carbazole, phenanthrene, and benzofuran (Steele, 1995).

1,4-Di-*tert*-butylbenzene is a solid at 298.15 K. By judicious choice of starting temperature, the melting endotherm during the DSC enthalpy measurements for 1,4-di-*tert*-butylbenzene 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 enthalpy of fusion at the melting point (350.8 K) and the corresponding value at 298.15 K are reported in Table 2. Equations, representing the heat capacities for the liquid and solid phases, 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.)

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 derived (Chirico and Steele, 1994), the expected accuracy of the densities is ±0.1 kg·m^{-3}.

Fitting Procedures. With the exception of 2-cyclohexen-1-one, (±)-2-ethyl-hexanoic acid, and sulfolane, in general, the same fitting procedures were used for all the remaining compounds of this study. Details of the fitting procedures used for the enone, the acid, and the sulfone are given at the end of this section. In general, the number of fitting parameters differed depending on whether or not a critical temperature could be determined experimentally. For 2-(methylamino)ethanol extensive sample decomposition precluded critical temperature measurements, and therefore, both T_c and p_c were included as variables. For cyclohexanol, 1,2-dichloropropane, 1,4-di-*tert*-butylbenzene, and perfluoro-*n*-heptane, 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 $C^{II}_{x,m}$ given in Table 2. A summary of the procedure follows.

The Wagner (1973) equation in the formulation highlighted by Ambrose and Walton (1989):

$$\ln(p/p_c) = (1/T_r)[AY + BY^{1.5} + CY^{2.5} + DY^5] \qquad (2)$$

where $T_r = T/T_c$, and $Y = (1 - T_r)$ was fitted to the measured vapor pressures (Table 1). As noted above, the critical pressure p_c [and, for 2-(methylamino)ethanol, the critical temperature T_c] was (were) included in the variables. The vapor-pressure fitting procedure including the minimization equation, and the relative weightings is detailed in Steele (1995).

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

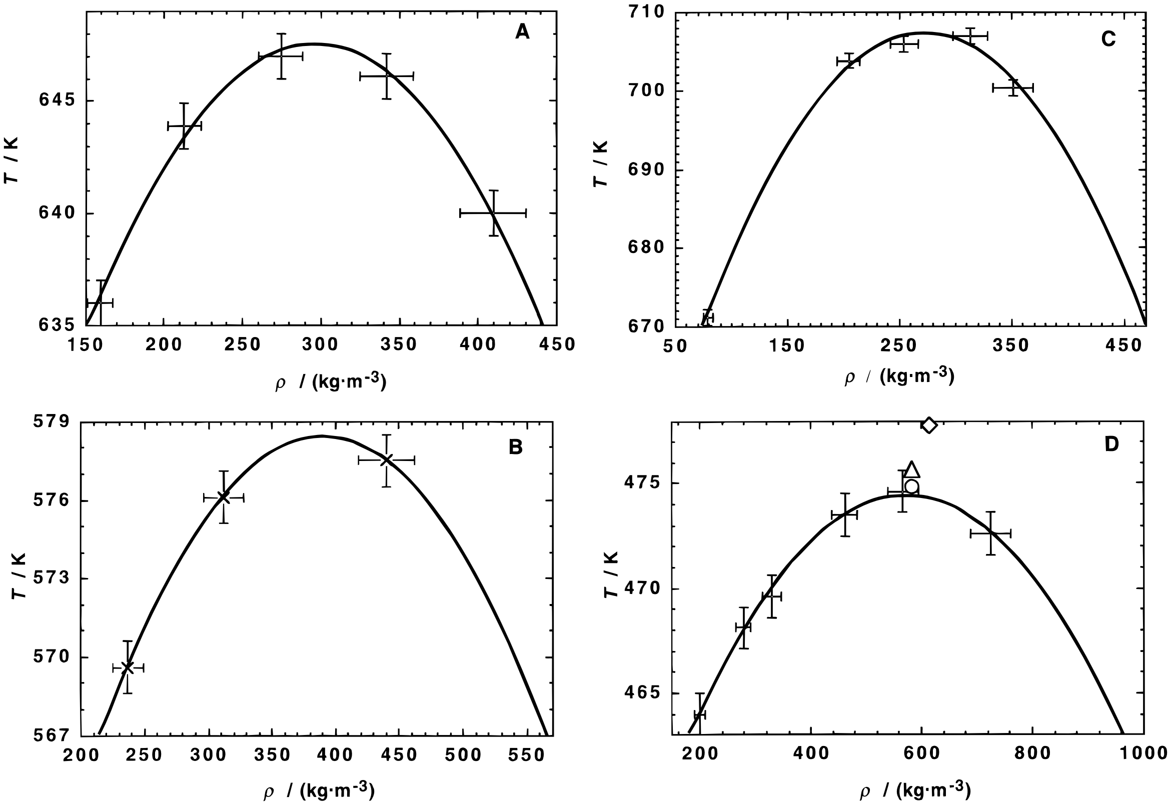

Figure 2. Vapor−liquid coexistence in the region of the critical point. A = cyclohexanol; B = 1,2-dichloropropane; C = 1,4-Di-*tert*-butylbenzene; D = perfluoro-*n*-heptane. The curves are drawn as an aid to the eye and do not represent any theoretically valid equation. The crosses span the range of uncertainty. Key: (△) Fowler et al. (1947); (○) Oliver et al. (1951); (◇) Ermakov and Skripov (1967).

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

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

The values of $C^{II}_{V,m}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{sat}$ and $(\partial^2\mu/\partial T^2)_{sat}$ [see eq 2 of Steele (1995)]. The functional form chosen for variation of the second derivative of the chemical potential with temperature was

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

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

Exceptions to the above procedures were made for 2-cyclohexen-1-one, (±)-2-ethylhexanoic acid, and sulfolane. All three compounds decomposed well removed from the critical region; measured vapor pressures covered a relatively narrow range of temperatures (Table 1), the measured $C^{II}_{x,m}$ values (Table 2) were virtually independent of cell filling. Hence, estimates were made for the critical temperatures. The critical pressures were selected with Waring's criterion for $T_r = 0.85$ (Waring, 1954). Application of this criterion was discussed recently by Steele (1995).

Derived Results. Table 5 lists the parameters derived using the procedures outlined above and in Steele et al. (1996b). Details of the fits using the vapor-pressure results are given in Table 1 (column 4 labeled $\Delta p = p - p_{Wagner}$, with p_{Wagner} calculated using the parameters listed in Table 5.).

Values of $C^{II}_{V,m}$ ($\rho = \rho_{sat}$) 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-equation fits (Table 5) using the Clapeyron equation

$$dp/dT = \Delta_l^g H_m/(T\,\Delta_l^g V_m) \qquad (5)$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. In earlier work in this project the liquid-phase density estimates were made with the extended corresponding-states equation (Riedel, 1954) as formulated by Hales and Townsend (1972)

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

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

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

has proved to be a better representation of the measured densities for a wide range of compound types from alkanes through compounds containing highly polar groups (Steele, 1996) with the exception of alcohols. Alcohols and other strongly hydrogen-bonding compounds are best represented by a power series in T (eq 7A) over the temperature range from the triple point to approximately 400 K (see below):

$$\rho = \text{constant} + AT + BT^2 + CT^3 \qquad (7A)$$

Estimates of the liquid-phase volumes were made using

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

T/K	ρ/(kg·m^{-3})	$100(\rho - \rho_{\mathrm{calc}})/\rho$
	Cyclohexanol[b]	
323.137	918.5	0.00
348.131	899.6	0.00
373.124	879.9	0.00
398.119	859.4	0.00
423.116	834.3	−0.42
448.112	804.1	−1.35
473.149	772.3	−2.41
	1,2-Dichloropropane[d]	
323.137	1112.8	−0.03
348.133	1081.4	0.09
373.124	1045.6	−0.09
398.119	1011.3	0.03
423.113	971.8	−0.19
	(±)-2-Ethylhexanoic Acid[f]	
323.148	891.3	0.00
348.130	870.1	0.00
373.126	848.6	0.00
398.116	827.5	−0.01
423.114	805.6	−0.25
448.112	777.6	−1.56
473.110	753.6	−2.78
	Perfluoro-*n*-heptane[h]	
323.147	1647.5	0.00
348.130	1571.7	0.00
373.121	1488.6	0.00
398.118	1394.4	0.00
	2-Cyclohexen-1-one[c]	
323.136	965.3	0.01
348.130	942.4	0.00
373.125	919.1	−0.02
398.121	896.0	−0.01
423.113	873.2	0.05
448.111	848.9	−0.02
	1,4-Di-*tert*-butylbenzene[e]	
373.125	805.9	0.07
398.118	785.7	−0.06
423.115	765.8	−0.08
448.112	745.7	−0.01
473.109	724.9	0.07
498.109	702.6	0.09
523.110	677.7	−0.08
	2-(Methylamino)ethanol[g]	
323.136	913.7	−0.02
348.130	895.0	0.06
373.123	872.9	−0.09
398.120	852.4	0.06
423.114	829.5	−0.02
	Sulfolane[i]	
323.151	1240.3	−0.04
348.130	1220.6	0.12
373.123	1197.0	−0.09
398.117	1176.6	−0.05

[a] ρ_{calc} values were calculated using eqs 7 or 7A and the parameters listed below. [b] $\rho_{\mathrm{calc}} = 1155.91 - 0.881\,02T + 9.247 \times 10^{-4}T^2 - 1.469 \times 10^{-6}T^3$. [c] $\rho_{\mathrm{calc}} = 315.0 + 1090.0(1 - T/685)^{1/3} - 1230.7\,(1 - T/685)^{2/3} + 1085.3\,(1 - T/685)$. [d] $\rho_{\mathrm{calc}} = 390.0 + 944.3(1 - T/577)^{1/3} - 428.0\,(1 - T/577)^{2/3} + 574.1\,(1 - T/577)$. [e] $\rho_{\mathrm{calc}} = 260.0 + 541.2(1 - T/708)^{1/3} + 55.5\,(1 - T/708)^{2/3} + 190.3\,(1 - T/708)$. [f] $\rho_{\mathrm{calc}} = 786.79 + 2.3383T + 8.903 \times 10^{-3}T^2 - 8.256 \times 10^{-6}T^3$. [g] $\rho_{\mathrm{calc}} = 768.91 + 2.2705T - 7.6155 \times 10^{-3}\,T^2 + 6.1189 \times 10^{-6}T^3$. [h] $\rho_{\mathrm{calc}} = 590.0 + 1375.5\,(1 - T/475)^{1/3} - 71.28\,(1 - T/475)^{2/3} + 469.9\,(1 - T/475)$. [i] $\rho_{\mathrm{calc}} = 1701.46 - 2.2813T + 3.6204 \times 10^{-3}T^2 - 3.0078 \times 10^{-6}T^3$.

either eq 7 or eq 7A 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 vaporization are reported in Table 7. For $p > 1$ bar the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization.

Solubility parameters are listed in Table 8.

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 DIPPR Project 801 Database (Daubert et al., 1994).

Comparison with Literature Values. Cyclohexanol. In agreement with the conclusions of Ambrose and Ghiassee (1987), measurements on cyclohexanol showed the compound to be unstable to *prolonged* heating above the normal boiling point. Glaser and Rüland (1957) reported a critical temperature (625 K) and critical pressure (3750 kPa) for cyclohexanol determined as part of a study of the vapor pressures of a number of industrially important compounds. As noted by Ambrose and Ghiassee (1987) in their study, Glaser and Rüland used a massive metal apparatus and it “seems doubtful whether the observations on unstable compounds could have been made sufficiently rapidly to avoid effects arising from decomposition.” The critical points were identified by Glaser and Rüland by the apparent discontinuity in the plot of $\ln(p/p°)$ against $1/T$. This is an insensitive method of deriving the critical temperature and critical pressure. Ambrose and Ghiassee (1987) obtained values for the critical properties by “graphical extrapolation of the observed values back to the beginning of the experiments.” They list derived values of $T_{\mathrm{c}} = (650 \pm 2)$ K, and $p_{\mathrm{c}} = (4260 \pm 50)$ kPa in good agreement with the values $T_{\mathrm{c}} = (648 \pm 1)$ K obtained during the DSC measurements, and $p_{\mathrm{c}} = (4075 \pm 100)$ kPa derived from the fitting procedures used in the research reported here. Measurements made within the DIPPR Project 851 and reported by Wilson et al. (1996) give $T_{\mathrm{c}} = (647.1 \pm 0.1)$ K and $p_{\mathrm{c}} = (4401 \pm 21)$ kPa for cyclohexanol from a study in a flow apparatus. The error limits for the Wiltec results seem optimistic even for compounds *stable* in the critical region.

Results from numerous studies of the vapor pressure of cyclohexanol have been reported in the literature (de Forcrand, 1912; Gardner and Brewer, 1937; Stull, 1947; Nitta and Seki, 1948; Glaser and Rüland, 1957; Novák et al., 1960; Hennings and Weber, 1962; Smith and Thorp, 1963; Goodwin and Newsham, 1974; Cabani et al., 1975; Ambrose and Ghiassee, 1987; Burguet et al., 1993). Figure 3A,B compares these results with values obtained using eq 2 and the parameters listed in Table 5. Figure 3A shows the excellent accord ($\pm 0.002 \cdot p$) between the results of Ambrose and Ghiassee (1987) and those of the present research. The results reported in de Forcrand (1912), Novák et al. (1960), Hennings and Weber (1962), and Burguet et al. (1993) all lie within the narrow band +1% to −2% of the values calculated using the Wagner equation and the parameters listed in Table 5 (see Figure 3A). It is worth noting that for cyclohexanol, measurements obtained in 1912 are as accurate as those obtained in 1993! For calculation of the vapor pressure of cyclohexanol, the

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

	Cyclohexanol				2-Cyclohexen-1-one		
A	−7.670 95	b_0	−0.543 69	A	−7.832 92		
B	3.193 08	b_1	0.819 93	B	2.377 18		
C	−8.342 13	b_2	−7.152 98	C	−2.891 34		
D	−5.828 88	b_3	9.455 84	D	−2.903 51		
T_c	648	p_c	4075	T_c	685	p_c	4530
ρ_c	300	ω	0.3662	ρ_c	315	ω	0.3084
	1,2-Dichloropropane				1,4-Di-*tert*-butylbenzene		
A	−7.705 57	b_0	−0.282 35	A	−9.284 68	b_0	−0.813 82
B	2.621 97	b_1	−0.603 31	B	3.892 31	b_1	−0.626 26
C	−2.741 04	b_2	0.868 26	C	−5.551 38	b_2	−0.015 65
D	−3.089 34	b_3	−1.317 19	D	−3.341 44	b_3	0.105 76
T_c	578	p_c	4650	T_c	708	p_c	2300
ρ_c	390	ω	0.2552	ρ_c	260	ω	0.5061
	(±)-2-Ethylhexanoic acid				2-(Methylamino)ethanol		
A	−10.816 36			A	−9.809 14	b_0	−0.319 95
B	5.785 60			B	4.941 30	b_1	−1.639 02
C	−12.537 20			C	−9.351 48	b_2	3.704 29
D	2.369 53			D	2.685 97	b_3	−3.359 46
T_c	675	p_c	2780	T_c	630	p_c	5300
ρ_c	260	ω	0.8030	ρ_c	290	ω	0.6039
	Perfluoro-*n*-heptane				Sulfolane		
A	−9.189 55	b_0	−0.934 41	A	−12.377 02		
B	3.151 38	b_1	−1.617 21	B	9.781 68		
C	−5.419 34	b_2	2.454 17	C	−6.999 53		
D	−4.111 74	b_3	−3.915 01	D	−1.911 45		
T_c	475	p_c	1650	T_c	855	p_c	7290
ρ_c	590	ω	0.5611	ρ_c	360	ω	0.5234

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

DIPPR Project 801 Database (Daubert et al., 1994) lists an equation that is represented by the dashed curve in Figure 3A. The Project 801 compilers refer to the measurements of Ambrose and Ghiassee (1987) as the sole source of their derived equation.

Results from the other studies (Gardner and Brewer, 1937; Stull, 1947; Nitta and Seki, 1948; Smith and Thorp, 1963; Goodwin and Newsham, 1974; Cabani et al., 1975) are shown in Figure 3B. All of those results differ significantly from the values calculated using the Wagner equation and the parameters listed in Table 5. Values listed by Glaser and Rüland (1957) are not shown in either plot. The values listed by Glaser and Rüland are 8.4% low at 461 K rising linearly with temperature to reach 12.6% high at 621 K.

Alcohols in general show strong hydrogen bonding in the liquid phase at temperatures below approximately 400 K. One manifestation of that fact can be seen in the relative constancy of their heat capacity over a wide temperature range as the hydrogen bonding is "broken-up" [see e.g., Figure 10 depicting the liquid-phase heat capacity of tetradecanol in Steele et al. (1991b)]. Careful scrutiny of the measured densities for cyclohexanol made using the vibrating tube densimeter showed that the measured values below 400 K formed a consistent set that deviated markedly from the two measurements made above that temperature. Note also that the derived $C_{\rm sat}$ values (Table 6) are relatively constant over the temperature range 440 K to 560 K, which compares well with that depicted in Figure 10 of Steele et al. (1991b). Due to the hydrogen bonding, any derived correlation of the liquid-phase densities should not hold for temperature greater than 400 K. In this research eq 8 was derived from a fit of the measurements made below 400 K and reported in Table 4.

$$\rho/(\mathrm{kg{\cdot}m^{-3}}) = 1155.91 - 0.88012{\cdot}T + 9.247 \times 10^{-4}{\cdot}T^2 - 1.469 \times 10^{-6}{\cdot}T^3 \quad (8)$$

Figure 4A,B compares values for the saturated liquid phase density of cyclohexanol found in a literature search (Richards and Shipley, 1916; Herz and Bloch, 1924; Velasco, 1927; Timmermans and Hennaut-Roland, 1937; Friend and Hargreaves, 1944; Kuss, 1955; Ravdel et al., 1970; Shinomiya, 1990) with values calculated using eq 8. [Only densities over a range of temperatures were abstracted from the literature. Numerous single-point values (usually at 303 K) were also found in the search but excluded from consideration.] Also included in the figures (represented by the dashed curve) is the equation given by the DIPPR Project 801 Database (Daubert et al., 1994), to represent the saturation liquid density for cyclohexanol. The DIPPR 801 Project Database representation of the variation of the saturation liquid density of cyclohexanol with temperature reproduces the literature values well. However, none of the values for the saturation liquid density available in the literature is in accord with the measurements reported in this research. Except for the Timmermans and Hennaut-Roland (1937) reference, no details are reported of the purities of the samples used in the earlier measurements. Timmermans and Hennaut-Roland noted that the presence of water and phenol (from which cyclohexanol is usually manufactured) as impurities would "probably elevate the density." The densities measured at NIPER on the pure (>99.97 mol %) cyclohexanol sample are lower, in agreement with the Timmermans and Hennaut-Roland assertion. Note that the Friend and Hargreaves (1944) values follow the deviation of the NIPER results as the temperature increases above 400 K. However, they deviate on the low side of the reported Table 4 measurements.

Table 9 gives a comparison of enthalpies of vaporization for cyclohexanol (de Forcrand, 1912; Mathews and Fehlandt, 1931; Nitta and Seki, 1948; Glaser and Rüland, 1957; Hennings and Weber, 1962; Wadsö, 1966; Cabani et al., 1975) with values derived in this research (see above and Table 7). All the literature values except Wadsö (1966) differ from values obtained in this research by amounts no greater than the estimated overall probable errors in the measurements. For Wadsö (1966), which is a measurement obtained with a vaporization calorimeter and not determined via the slope of a vapor pressure versus

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	$C_{\mathrm{sat,m}}/R$
	Cyclohexanol		
300.0	25.3	480.0	38.3
320.0	28.3	500.0	38.2
340.0	30.9	520.0	38.1
360.0	33.1	540.0	38.1
380.0	34.8	560.0	38.4
400.0	36.2	580.0	39.1
420.0	37.2	600.0	40.6
440.0	37.8	620.0	43.4
460.0	38.1		
	1,4-Di-*tert*-butylbenzene		
360.0	47.4	540.0	62.7
380.0	49.5	560.0	64.2
400.0	51.5	580.0	65.8
420.0	53.3	600.0	67.5
440.0	55.1	620.0	69.5
460.0	56.7	640.0	71.9
480.0	58.3	660.0	75.3
500.0	59.8	680.0	81.1
520.0	61.3		
	1,2-Dichloropropane		
300.0	18.8	460.0	22.6
320.0	19.2	480.0	23.3
340.0	19.6	500.0	24.0
360.0	20.1	520.0	25.0
380.0	20.5	540.0	26.8
400.0	21.0	560.0	31.3
420.0	21.5	570.0	39.6
440.0	22.1		
	2-(Methylamino)ethanol		
300.0	23.3	480.0	32.5
320.0	24.2	500.0	33.3
340.0	25.3	520.0	34.0
360.0	26.3	540.0	34.5
380.0	27.4	560.0	34.9
400.0	28.5	580.0	35.6
420.0	29.6	600.0	37.7
440.0	30.6	620.0	49.3
460.0	31.6		
	Perfluoro-*n*-heptane		
300.0	50.5	400.0	57.5
320.0	51.8	420.0	59.2
340.0	53.2	440.0	61.5
360.0	54.6	460.0	67.8
380.0	56.1	470.0	83.5

Table 7. Enthalpies of Vaporization Obtained from the Wagner and Clapeyron Equations^a

T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}
	Cyclohexanol		
298.15^b	63.48 ± 0.67	420.0	46.58 ± 0.40
300.0^b	63.22 ± 0.67	440.0	43.76 ± 0.47
320.0^b	60.34 ± 0.57	460.0	40.89 ± 0.60
340.0^b	57.54 ± 0.50	480.0^b	37.97 ± 0.75
360.0	54.79 ± 0.45	500.0^b	35.03 ± 0.93
380.0	52.07 ± 0.40	520.0^b	32.1 ± 1.1
400.0	49.34 ± 0.38		
	1,2-Dichloropropane		
260.0^b	38.35 ± 0.25	360.0	32.73 ± 0.25
280.0^b	37.19 ± 0.22	380.0	31.55 ± 0.33
298.15	36.17 ± 0.22	400.0	30.33 ± 0.42
300.0	36.07 ± 0.20	420.0^b	29.01 ± 0.55
320.0	34.96 ± 0.20	440.0^b	27.60 ± 0.70
340.0	33.86 ± 0.22	460.0^b	26.07 ± 0.86
	2-Cyclohexen-1-one		
280.0^b	49.46 ± 0.35	420.0	41.46 ± 0.30
298.15^b	48.36 ± 0.33	440.0	40.27 ± 0.35
300.0^b	48.25 ± 0.33	460.0	39.03 ± 0.42
320.0^b	47.08 ± 0.30	480.0	37.72 ± 0.53
340.0	45.94 ± 0.28	500.0^b	36.33 ± 0.67
360.0	44.82 ± 0.27	520.0^b	34.82 ± 0.81
380.0	43.71 ± 0.27	540.0^b	33.2 ± 1.0
400.0	42.60 ± 0.27		
	1,4-Di-*tert*-butylbenzene		
298.15^{b,c}	62.97 ± 0.57	470.0	49.00 ± 0.42
330.0^{b,c}	60.23 ± 0.50	490.0	47.28 ± 0.48
350.0^{b,c}	58.58 ± 0.47	510.0	45.49 ± 0.60
370.0b	56.96 ± 0.43	530.0	43.59 ± 0.75
390.0	55.38 ± 0.40	550.0	41.58 ± 0.93
410.0	53.81 ± 0.37	570.0^b	39.4 ± 1.2
430.0	52.24 ± 0.37	590.0^b	37.1 ± 1.4
450.0	50.64 ± 0.37	610.0^b	34.6 ± 1.7
	(±)-2-Ethylhexanoic acid		
298.15^b	76.31 ± 0.93	460.0	59.87 ± 0.53
340.0^b	72.81 ± 0.78	480.0	57.14 ± 0.57
360.0^b	70.97 ± 0.72	500.0	54.19 ± 0.68
380.0^b	69.03 ± 0.67	520.0^b	51.03 ± 0.86
400.0	66.96 ± 0.62	540.0^b	47.7 ± 1.1
420.0	64.76 ± 0.57	560.0^b	44.1 ± 1.4
440.0	62.41 ± 0.53		
	Perfluoro-*n*-heptane		
260.0^b	39.56 ± 0.30	360.0	30.38 ± 0.55
280.0^b	37.85 ± 0.28	380.0	28.09 ± 0.76
298.15^b	36.29 ± 0.27	400.0^b	25.5 ± 1.0
300.0	36.13 ± 0.27	420.0^b	22.6 ± 1.3
320.0	34.35 ± 0.30	440.0^b	19.2 ± 1.7
340.0	32.45 ± 0.40		
	2-(Methylamino)ethanol		
298.15^b	57.00 ± 0.52	400.0	50.23 ± 0.38
300.0^b	56.91 ± 0.50	420.0	48.39 ± 0.40
320.0^b	55.86 ± 0.47	440.0	46.35 ± 0.47
340.0	54.67 ± 0.45	460.0	44.10 ± 0.58
360.0	53.35 ± 0.42	480.0^b	41.65 ± 0.76
380.0	51.87 ± 0.40	500.0^b	39.0 ± 1.0
	Sulfolane		
298.15^{b,c}	67.77 ± 0.80	480.0	56.85 ± 0.33
360.0^b	63.79 ± 0.45	500.0	55.80 ± 0.33
380.0^b	62.55 ± 0.42	520.0	54.78 ± 0.33
400.0^b	61.34 ± 0.40	540.0	53.79 ± 0.37
420.0^b	60.17 ± 0.38	560.0^b	52.82 ± 0.40
440.0	59.03 ± 0.35	580.0^b	51.88 ± 0.47
460.0	57.93 ± 0.33	600.0^b	50.95 ± 0.55

[a] Uncertainty intervals are twice the standard deviation. [b] The value at this temperature was calculated with extrapolated vapor pressures derived from the fitted Wagner equation. [c] This temperature was below the melting point, and hence the enthalpy value is for the hypothetical metastable liquid phase.

temperature plot, the difference is outside the sum of the error bands. This may denote an error in the extrapolated slope arising from small errors in the Wagner parameters listed in Table 5 for cyclohexanol [a similar problem with the results for another hydrogen-bonded compound, hexane-1,6-diol, was resolved in Steele et al. (1996c) by vapor pressure measurements in the low-pressure (inclined piston) region].

2-Cyclohexen-1-one. In contrast to cyclohexanol, virtually no articles relating thermochemical or thermophysical property measurements on 2-cyclohexen-1-one were found during a search of the literature. An on-line computer search using the Beilstein database revealed nine single-point density measurements, seven of which were at 293 K. The seven densities at 293 K spanned the range 980 kg·m^{-3} (Prevost-Gangneaux et al., 1966) to 996.2 kg·m^{-3} (Whitmore and Pedlow, 1941). Using eq 7 and the parameters listed in the footnotes to Table 4, a ρ_{sat}(293 K) = 992.6 kg·m^{-3} is calculated. The Beilstein database search revealed 48 references to the boiling point of 2-cyclohexen-1-one covering the pressure range 0.5 kPa to 101.325 kPa. All of these values were determined during synthesis of the compound.

1,2-Dichloropropane. In the research reported here, values of T_c = 578 K and ρ_c = 390 kg·m^{-3} were determined from the DSC measurements and p_c = 4650 kPa was derived using the fitting procedures (see Figure 2 and Table 4). The Project 801 Database (Daubert et al., 1994) lists a

Table 8. Solubility Parameters[a,b]

compound	ρ/mol·m^{-3}	$\Delta_l^g U_m$/J·mol^{-1}	δ/(J·m^{-3})$^{1/2}$
cyclohexanol	9230	61 000	2.37×10^4
2-cyclohexen-1-one	10250	45 880	2.17×10^4
1,2-dichloropropane	10135	33 700	1.85×10^4
1,4-di-*tert*-butylbenzene	4315	55 580	1.55×10^4
(±)-2-ethylhexanoic acid	6316	73 830	2.16×10^4
2-(methylamino)ethanol	12468	54 520	2.61×10^4
perfluoro-*n*-heptane	4448	33 810	1.23×10^4
sulfolane	10473	65 170	2.61×10^4

[a] Densities (listed to an extra significant figure to prevent round off errors) were estimated by extrapolation of the equations listed in the footnotes to Table 4. [b] $\Delta_l^g U_m = (\Delta_l^g H_m - R \cdot T)$ obtained using the values for the enthalpy of vaporization at 298.15 K (or in the cases of 1,4-di-*tert*-butylbenzene and sulfolane at the melting point). [c] The melting point of 1,4-di-*tert*-butylbenzene was 350.8 K. The melting point of sulfolane was 300.6 K.

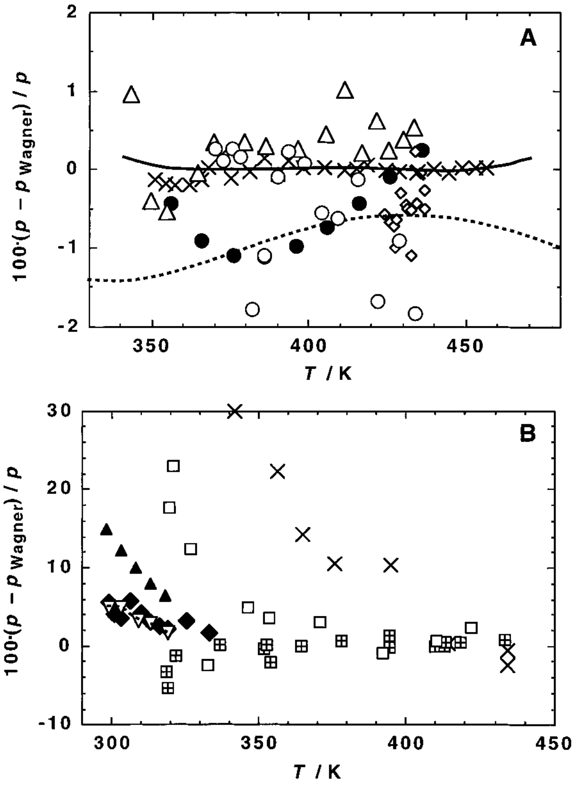

Figure 3. (A) Comparison of literature vapor pressures for cyclohexanol with values obtained using the Wagner equation (eq 2) and the parameters listed in Table 5. The solid line represents the deviations listed in Table 1. The dashed line represents the deviations obtained using the DIPPR 801 Project Database (Daubert et al., 1994). Key: (◇) de Forcrand (1912); (○) Novák et al. (1960); (×) Ambrose and Ghiassee (1987); (●) Hennings and Weber (1962); (△) Burguet et al. (1993); (B) Comparison of literature vapor pressures for cyclohexanol with values obtained using the Wagner equation (eq 2) and the parameters listed in Table 5. Key: (△) Gardner and Brewer (1937); (×) Stull (1947); (◆) Nitta and Seki (1948); (▲) Smith and Thorp (1963); (square with +) Goodwin and Newsham (1974); (▽) Cabani et al. (1975).

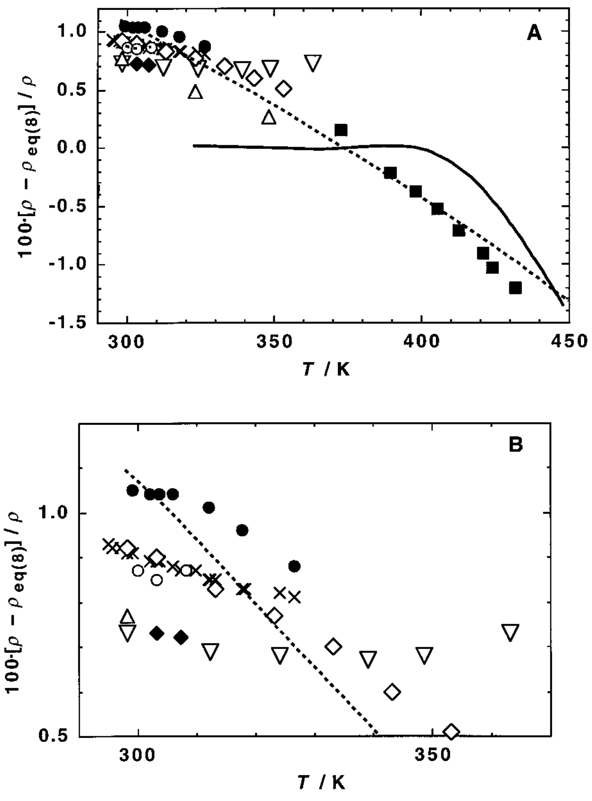

Figure 4. (A) Comparison of literature saturation liquid densities for cyclohexanol with values obtained using eq 8. The solid line represents the deviations for the densities listed in Table 4. The dashed line represents the deviations obtained using the DIPPR 801 Project Database (Daubert et al., 1994). Key: (◆) Richards and Shipley (1916); (▽) Herz and Bloch (1924); (●) Velasco (1927); (×) Timmermans and Hennaut-Roland (1937); (■) Friend and Hargreaves (1944); (◇) Kuss (1955); (△) Ravdel et al. (1970); (○) Shinomiya (1990). (B) "Blowup" of the "low" temperature section of the comparison in Figure 5A.

dozen references to measurements of the vapor pressure of 1,2-dichloropropane which were used to derive their correlation for the vapor pressure between the triple point and critical point. However, most are data compilations and single-point determinations during syntheses of the compound. Only three (Nelson and Young, 1933; Dreisbach and Shrader, 1949; Varushchenko et al., 1982) contain vapor pressure measurements over a range of temperature. Figure 5 compares the Project 801 Database (Daubert et al., 1994) correlation and the results obtained by Nelson and Young (1933), Dreisbach and Shrader (1949), and Varushchenko et al. (1982) with values for the vapor pressure of 1,2-dichloropropane obtained using eq 2 and the parameters listed in Table 5. Agreement between the sets of measurements is good except for those of Nelson and Young (1933) below ~320 K.

Figure 6 compares ρ_{sat} values for 1,2-dichloropropane found in the literature (Nelson and Young, 1933; Vogel, 1948; Lagemann et al., 1949; Dreisbach and Martin, 1949) with values calculated using eq 7 and the parameters listed in the footnotes to Table 4. The deviations shown are large. The DIPPR 801 Project representation of the variation of the density ρ_{sat} of 1,2-dichloropropane (the dotted curve in Figure 6) reproduces the limited range of literature values.

Table 9 gives a comparison of enthalpies of vaporization for 1,2-dichloropropane found in the literature (Nelson and Young, 1933; Varushchenko et al., 1982) with values derived in this research (Table 7). Differences are within the estimated overall probable errors in the measurements.

1,4-Di-tert-butylbenzene. No thermophysical property measurements on 1,4-di-*tert*-butylbenzene were found in a search of the chemical literature through January 1997. In addition to the suite of measurements and derived properties reported in the present research (ebulliometric vapor pressures, 2−270 kPa; densities along the saturation line, 373 to 523 K; heat capacities, 300 to 630 K; $T_c = (708 \pm 1)$ K; $p_c = (2300 \pm 100)$ kPa; $\rho_c = (260 \pm 10)$ kg·m^{-3}; enthalpies of fusion, at the melting point 350.8 K, and at 298.15 K; and enthalpies of vaporization, 298.15 to 610 K)

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

reference	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	Δ/kJ·mol^{-1} [a]
Cyclohexanol			
de Forcrand (1912)	48.9	433.0	4.1
Mathews and Fehlandt (1931)	45.5 ± 0.1	431.9	0.6
Nitta and Seki (1948)	60.3	316.2	−0.6
Glaser and Rüland (1957)	42.4	433.7	−2.2
Hennings and Weber (1962)	45.4	434.0	0.7
	46.9	420.8	0.4
	53.9	361.6	−0.7
Wadsö (1966)	62.0 ± 0.3	298.15	−1.5
Cabani et al. (1975)	62.0 ± 0.9	298.15	−1.5
1,2-Dichloropropane			
Nelson and Young (1933)	34.3	308	−1.3
	34.2	348	0.8
Varushchenko et al. (1982)	36.36 ± 0.42	298.15	0.2
(±)-2-Ethylhexanoic acid			
Stridh (1976)	75.60 ± 0.42	298.15	−0.7
Perfluoro-*n*-heptane			
Fowler et al. (1947)	34.5	321	0.2
Oliver and Grisard (1951)	36.34	298.15	0.05
	31.56	355.65	0.70
Ermakov and Skripov (1969)	40.4	343	8.2
	33.3	373	4.4
	26.5	403	1.4
	19.7	433	−0.8
	12.8	463	−1.2
Sulfolane			
Walker (1952)	73.3	293	5.2
Deal et al. (1959)	62.8	373	−0.2
	61.6	473	4.4
Tanginov et al. (1992)	56.9	558.3	4.0
	51.3	558.3	−1.7

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

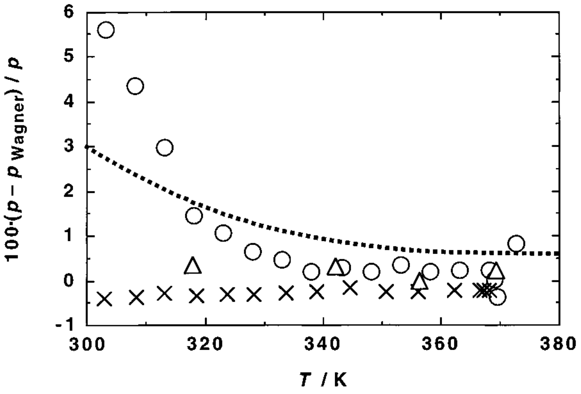

Figure 5. Comparison of literature vapor pressures for 1,2-dichloropropane with values obtained using the Wagner equation (eq 2) and the parameters listed in Table 5. The vapor pressure measurements obtained in this research (see Table 1) span the temperature range 293 to 406 K. The dashed line represents the deviations obtained using the DIPPR 801 Project Database (Daubert et al., 1994). Key: (○) Nelson and Young (1933); (△) Dreisbach and Shrader (1949); (×) Varushchenko et al., (1982).

further heat-capacity measurements in the temperature range 4 < T/K < 450 K by adiabatic calorimetry, inclined piston manometry in the pressure range 0.02 to 3.0 kPa, and a determination of the energy of combustion are scheduled for this compound within a research program funded by U.S. DOE Fossil Energy. There is at present a lack of thermochemical and thermophysical property measurements on compounds containing *tert*-butyl groups. Results obtained for this compound will be used to reinforce group additivity calculations on compounds containing this important group.

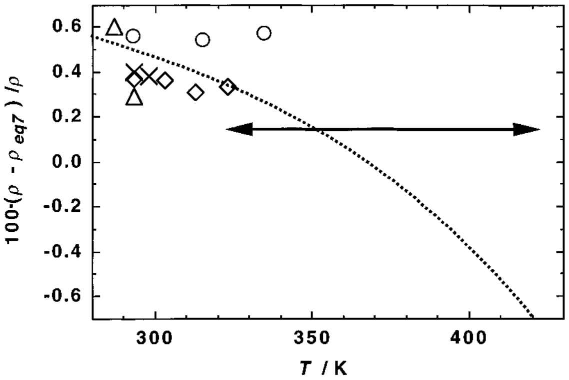

Figure 6. Comparison of literature saturation liquid densities for 1,2-dichloropropane with values obtained using eq 7 and the parameters listed in footnote d to Table 4. The double-headed arrow represents the temperature span of the density measurements obtained in this research (see Table 4). The dashed line represents the deviations obtained using the DIPPR 801 Project Database (Daubert et al., 1994). Key: (△) Nelson and Young (1933); (●) Vogel (1948); (◇) Lagemann and McMillan (1949); (×) Dreisbach and Martin (1949).

(±)-2-Ethylhexanoic Acid. Onset of sample decomposition was noted in the ebulliometric vapor pressure measurements for (±)-2-ethylhexanoic acid above 507 K. The rapid heating method used previously for critical temperature and critical density determinations (Steele, 1995) proved unsuccessful for the determination of the critical properties of (±)-2-ethylhexanoic acid. Hence, both the critical temperature and the critical pressure were included as variables in the fitting procedures described above. After the fitting was complete, two recent references to the determination of the critical properties of (±)-2-ethylhexanoic acid were found in the literature, Teja and Anselme (1990) and Teja and Rosenthal (1990). Both determinations were made in research funded by the DIPPR 851 Project. Values of T_c determined in the experimental measurements of (673.6 ± 1.2) K (Teja and Anselme, 1990) and (674.6 ± 0.6) K (Teja and Rosenthal, 1990) are in excellent agreement with the recommended value derived in the NIPER research, (675 ± 5) K. The critical pressure was measured during the Teja and Rosenthal (1990) study, p_c = (2778 ± 30) kPa [cf. a value of (2780 ± 300) kPa derived here]. The measured critical density ρ_c = (273 ± 5) kg·m^{-3} compares with a value of (260 ± 15) kg·m^{-3} derived here.

The DIPPR Project 801 Database (Daubert et al., 1994) lists eight references to measurements of the vapor pressure of (±)-2-ethylhexanoic acid, which were used in the derivation of their correlation for the vapor pressure between the triple and critical points. However, those references are to data compilations and single-point determinations during syntheses of the compound. A search of the literature since 1930 found only one additional reference containing vapor-pressure measurements (Schechter and Brain, 1963). Schechter and Brain list vapor pressures of 0.13 kPa at 356 K and 4.67 kPa for the temperature range 369−370 K. Corresponding pressures calculated using eq 2 and the parameters listed in Table 5 are 0.175 kPa at 356 K, 0.407 kPa at 369 K, and 0.433 kPa at 370 K, respectively. Notwithstanding the poor values reported in the open literature, agreement between the DIPPR Project 801 Database correlation and the experimentally measured values is good (±0.04·p) within the temperature range 400 < T/K < 650.

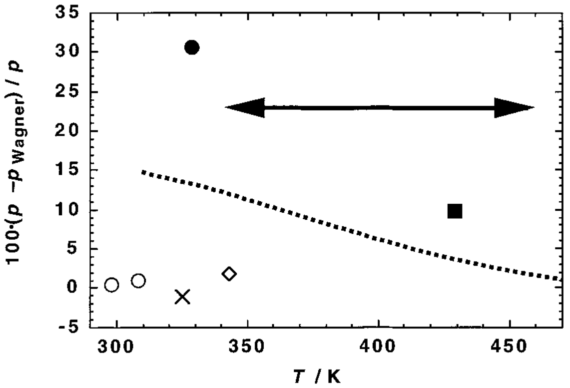

Figure 7. Comparison of literature vapor pressures for 2-(methylamino)ethanol with values obtained using the Wagner equation (eq 2) and the parameters listed in Table 5. The double-headed arrow represents the temperature span of the vapor pressure measurements obtained in this research (see Table 1). The dashed line represents the deviations obtained using the DIPPR 801 Project Database (Daubert et al., 1994). Key: (×) Hanby and Rydon (1947); (●) Adkins and Billica (1948); (■) Nikolaev et al. (1963); (◇) Mathis et al. (1970); (○) Touhara et al. (1982).

Like alcohols (see cyclohexanol above), acids also show strong hydrogen bonding in the liquid phase at temperatures below approximately 400 K. Careful scrutiny of the measured densities for (±)-2-ethylhexanoic acid made using the vibrating tube densimeter showed that the measured values below 400 K formed a consistent set that deviated markedly from the three measurements made above that temperature. Due to the hydrogen bonding, any derived low-temperature correlation of the liquid-phase densities should not hold for temperature greater than 400 K. In this research eq 9 was derived from a fit of the measurements made below 400 K and reported in Table 4:

$$\rho/(\mathrm{kg{\cdot}m^{-3}}) = 786.79 + 2.3383{\cdot}T - 8.903 \times 10^{-3}{\cdot}T^2 + 8.256 \times 10^{-6}{\cdot}T^3 \quad (9)$$

Values of the saturation liquid density of (±)-2-ethylhexanoic acid at 293 K and 298 K given by Stridh (1976) are both 1% lower than those determined using eq 9. Stridh noted that 2-ethylhexanoic acid "is very hygroscopic and had to be rigorously protected against water." The sample used in the combustion calorimetric study (Stridh, 1976) contained approximately 0.2% water. The sample used in the research reported here was 99.97 mol % pure.

Stridh (1976) lists an enthalpy of vaporization $\Delta_l^g H_m$ at 298.15 K for 2-ethyl-hexanoic acid (75.60 ± 0.42) kJ·mol^{-1} determined using a vaporization calorimeter (see Table 9). Agreement with the value derived in this research, (76.31 ± 0.93) kJ·mol^{-1}, is excellent.

2-(Methylamino)ethanol. The DIPPR Project 801 Database (Daubert et al., 1994) lists critical properties for 2-(methylamino)ethanol (T_c = 630 K, p_c = 5220 kPa, and ρ_c = 297 kg·m^{-3}) that are estimates. Sample decomposition prevented measurement of critical properties in this research. The fitting procedures used in this research provide values of T_c = (630 ± 10) K, p_c = (5300 ± 500) kPa, and ρ_c = (290 ± 20) kg·m^{-3}.

Figure 7 compares the Project 801 Database (Daubert et al., 1994) correlation and results listed in the following references (Hanby and Rydon, 1947; Adkins and Billica, 1948; Nikolaev et al., 1963; Mathis et al., 1970; Touhara et al., 1982) with values for the vapor pressure of 2-(methylamino)ethanol obtained using eq 2 and the parameters listed in Table 5. Except for the values of Adkins and Billica (1948) and Nikolaev et al. (1963) agreement among the various results is good.

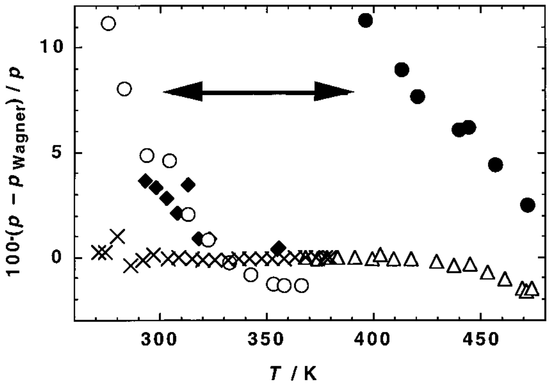

Figure 8. Comparison of literature vapor pressures for perfluoro-*n*-heptane with values obtained using the Wagner equation (eq 2) and the parameters listed in Table 5. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (see Table 1). Key: (○) Fowler et al. (1947); (×) Oliver and Grisard (1951); (△) Milton and Oliver (1952); (◆) Glew and Reeves (1956); (●) Ermakov and Skripov (1967).

Equation 10 was derived from a fit of the saturation liquid densities for 2-(methylamino)ethanol made below 400 K and reported in Table 4:

$$\rho/(\mathrm{kg{\cdot}m^{-3}}) = 768.91 + 2.2705{\cdot}T - 7.6155 \times 10^{-3}{\cdot}T^2 + 6.1189 \times 10^{-6}{\cdot}T^3 \quad (10)$$

Only two single-point values were obtained in a search of the literature: a value of 937 kg·m^{-3} at 293 K (Nikolaev et al., 1963) and 935.89 kg·m^{-3} at 298 K (Touhara et al., 1982), which compare with extrapolated values of 934 kg·m^{-3} and 931 kg·m^{-3}, respectively, obtained using eq 10.

Perfluoro-n-heptane (Hexadecafluoro-n-heptane). Fowler et al. (1947) measured critical properties for perfluoro-*n*-heptane using the disappearance of the meniscus method. The critical pressures of perfluoro-*n*-heptane and two other fluorocarbons were not determined, "but approximate values were calculated from the vapor pressure−temperature relations, assuming the heat of vaporization to be constant over the entire range." Fowler et al. noted that the enthalpy of vaporization "must decrease to zero at the critical point" and the critical pressures are "approximate values which should be upper limits for the pressure." Fowler et al. list T_c = (475.6 ± 0.2) K and p_c = 1925 kPa for perfluoro-*n*-heptane. Oliver et al. (1951) using an apparatus similar to that of Kay (1947) obtained T_c = (474.85 ± 0.05) K and p_c = (1621 ± 2) kPa. In addition, Oliver et al. (1951) lists a critical density of 584 kg·m^{-3} for perfluoro-*n*-heptane. Milton and Oliver (1952) measured the vapor pressure of perfluoro-*n*-heptane in the region of the critical point. A pressure−temperature plot of the experimental data in the region of the critical point resulted in a line whose slope approached infinity at a temperature T_c = (474.65 ± 0.1) K and a pressure p_c = (1613 ± 14) kPa. Ermakov and Skripov (1967) measured the critical constants T_c = (477.8 ± 0.2) K, p_c = (1750 ± 10) kPa, and ρ_c = 614 kg·m^{-3}. In the research reported here, values of T_c = 475 K and ρ_c = 588.7 kg·m^{-3} were determined from the DSC measurements and p_c = 1650 kPa was derived using the fitting procedures (see Figure 2 and Table 4).

Figure 8 compares vapor pressure measurements (Fowler et al., 1947; Oliver and Grisard, 1951; Milton and Oliver, 1952; Glew and Reeves, 1956; Ermakov and Skripov, 1967)

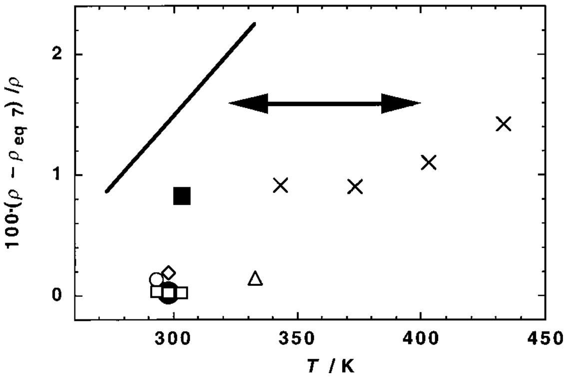

Figure 9. Comparison of literature saturation liquid densities for perfluoro-*n*-heptane with values calculated using eq 7 and the parameters listed in the footnote h to Table 4. The double-headed arrow represents the temperature span of the density measurements obtained in this research (see Table 4). The solid line represents the deviations obtained using Haszeldine and Smith (1951). Key: (○) Fowler et al. (1947); (△) Lagemann et al. (1948); (◇) Lagemann (1949); (□) Oliver et al. (1951); (●) Glew and Reeves (1956); (■) Skripov and Firsov (1968); (×) Ermakov and Skripov (1969).

with values for the vapor pressure of perfluoro-*n*-heptane obtained using eq 2 and the parameters listed in Table 5. The results of Fowler et al. (1947), Glew and Reeves (1956), and Ermakov and Skripov (1967) deviate markedly from the measurements reported here. Agreement between the results of Oliver and Grisard (1951) and those obtained in this research is excellent (maximum deviation 0.0012·*p* at 320 K) within the range of overlap of the vapor-pressure measurements (303 to 379 K). At lower temperatures (less than 300 K) agreement is not as good and reaches a peak of 0.01·*p* at 280 K. The low end of the Oliver and Grisard (1951) measurements appears to be in error and deviated markedly from the Antoine equation given in the text of the 1951 paper. Agreement between the results of Milton and Oliver (1952) and those obtained in this research is excellent (maximum deviation 0.0007·*p*) within the range of overlap of the vapor-pressure measurements (368 to 379 K). Up to the critical point the maximum difference is only 0.016·*p*, well within the uncertainty assigned to the critical pressure.

Figure 9 compares values for the saturated liquid-phase density of perfluoro-*n*-heptane found in a literature search (Fowler et al., 1947; Lagemann et al., 1948; Lagemann, 1949; Oliver et al., 1951; Haszeldine and Smith, 1951; Glew and Reeves, 1956; Skripov and Firsov, 1968; Ermakov and Skripov, 1969) with values calculated using values calculated using eq 7 and the parameters listed in the footnotes to Table 4. Agreement among the results of Fowler et al. (1947), Lagemann et al. (1948), Lagemann (1949), Oliver et al. (1951), and Glew and Reeves (1956) is excellent within ±0.002·*ρ* across the narrow temperature range. Both the values of Haszeldine and Smith (1951) and the Russian results (Skripov and Firsov, 1968; Ermakov and Skripov, 1969) are in serious disagreement with the rest of the available measurements. Ermakov and Skripov (1969) set an error limit of 0.01·*ρ* in their saturation liquid density measurements.

Several enthalpies of vaporization $\Delta_l^g H_m$ for perfluoro-*n*-heptane have been reported (Fowler et al., 1947; Oliver and Grisard, 1951; Ermakov and Skripov, 1969) (see Table 9). Fowler et al. (1947) calculated their value using the "integrated Clapeyron−Clausius equation", and in Table 9 the enthalpy of vaporization is assumed to apply at the midtemperature of the vapor pressure measurements (321 K). Oliver and Grisard (1951) used their critical constants and the Berthelot equation of state to calculate the two enthalpies of vaporization listed in Table 9. Ermakov and Skripov (1969) calculated their values from "the Clausius−Clapeyron equation, and the surface tension *σ* from the capillary constant." Agreement with values derived in this research (see column 4 of Table 9) is within the probable combined uncertainty intervals.

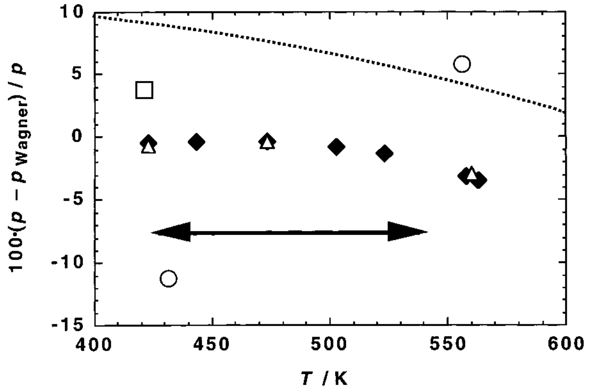

Figure 10. Comparison of literature vapor pressures for sulfolane with values obtained using the Wagner equation (eq 2) and the parameters listed in Table 5. The double-headed arrow represents the temperature span of the vapor pressure measurements obtained in this research (see Table 1). The dashed line represents the deviations obtained using the DIPPR 801 Project Database (Daubert et al., 1994). Key: (○) Jordan and Kipnis (1949); (□) Horner et al. (1958); (△) Deal et al. (1959); (◆) Morrow (1969).

Sulfolane. The DIPPR Project 801 Database (Daubert et al., 1994) lists three references to measurements of the vapor pressure of sulfolane Jordan and Kipnis (1949), Horner et al. (1958), and Deal et al. (1959). A search of the literature through January 1997 produced, in addition to numerous single-point boiling temperature at reduced pressure values, vapor-pressure measurements by Benoit and Choux (1968), Morrow (1969), and Ashcroft et al. (1979). Figure 10 compares the DIPPR Project 801 Database correlation (Daubert et al., 1994) and the results listed in Jordan and Kipnis (1949), Horner et al. (1958), Deal et al. (1959), and Morrow (1969) with values for the vapor pressure of sulfolane obtained using eq 2 and the parameters listed in Table 5. Agreement among the measurements of Horner et al. (1958), Deal et al. (1959), and Morrow (1969) and the results obtained in this research is good. The two points given by Jordan and Kipnis (1949) are in poor agreement. Using the Wagner equation (eq 2) and the parameters listed in Table 5, much lower vapor pressures are calculated in the region 303 to 328 K than those measured by either Benoit and Choux or Ashcroft et al. For example, at 303.15 K, Benoit and Choux measure the vapor pressure of sulfolane as 2.7 Pas, Ashcroft et al. obtained 9.1 Pas, and the Wagner equation fit gives a value of 1.4 Pas.

Figure 11A,B compares the DIPPR 801 Project Database representation of the temperature variation of the saturation liquid density of sulfolane with values calculated using eq 11:

$$\rho/(\mathrm{kg\cdot m^{-3}}) = 1701.46 - 2.2813\cdot T + 3.6204\times 10^{-3}\cdot T^2 - 3.0078\times 10^{-6}\cdot T^3 \quad (11)$$

Included in the figure are values for the saturated liquid-phase density of sulfolane found in a literature search (Deal et al., 1959; Jeffery et al., 1961; Lamanna et al., 1964; Vaughn and Hawkins, 1964; Sacco and Jannelli, 1972; Casteel and Sears, 1974; Sacco and Rakshit, 1975; Mur-

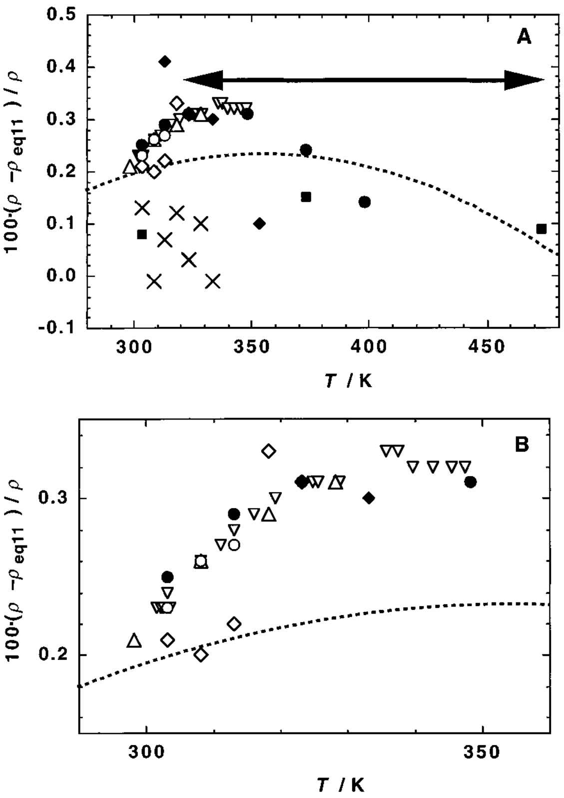

Figure 11. (A) Comparison of literature saturation liquid densities for sulfolane with values calculated using eq 11. The double-headed arrow represents the temperature span of the density measurements obtained in this research (see Table 4). The dashed line represents the deviations obtained using the DIPPR 801 Project Database (Daubert et al., 1994). Key: (■) Deal et al. (1959); (◆) Jeffery et al. (1961); (▽) Lamanna et al. (1964); (◇) Vaughn and Hawkins (1964); (△) Sacco and Jannelli (1972); (●) Casteel and Sears (1974); (○) Sacco and Rakshit (1975); (×) Murrieta-Guevara and Rodrîguez (1984). (B) "Blowup"of the 290 K to 360 K section.

rieta-Guevara and Rodrîguez, 1984). Only densities over a range of temperature were abstracted from the literature. Numerous single-point values (usually at 303 K) were also found in the search but excluded from consideration. Except for the measurements above 350 K, agreement between the measurements made in this research and values listed in the literature is poor. Some of the literature values are for the supercooled liquid below the melting point (303.6 K).

Walker (1952), Deal et al. (1959), and Tanginov et al. (1992) list enthalpies of vaporization $\Delta_l^g H_m$ for sulfolane (see Table 9). Agreement with values derived in this research (see column 4 of Table 9) is within the probable combined uncertainty intervals. There is excellent agreement (maximum deviation 1.7 kJ·mol^{-1} at 460 K) between the enthalpies of vaporization for sulfolane listed in Table 7 and values derived using the correlation listed in the DIPPR 801 Project Database.

There is also excellent agreement (maximum deviation 0.3R at 435 K) between the saturation heat capacities determined in the DSC measurements (listed in Table 2) and values derived using the correlation equation listed in the DIPPR 801 Project Database. Extensive sample decomposition below 600 K prevented verification of the correlation equation to the upper temperature limit of 711.15 K listed in the Database. Deal et al. (1959) list heat capacities at 303 K, 373 K, and 473 K, which are on average 15% lower than the values derived in this research.

Decomposition Points and Bond Dissociation Energies. 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:

$$\mathrm{BDE} = 64.7 \cdot R \cdot T \tag{12}$$

where BDE = bond dissociation energy, R = the gas constant, and T = the temperature of the onset of thermal decomposition. The onset of decomposition was noted for sulfolane at approximately 542 K during the ebulliometric vapor-pressure measurements. Applying that rule in this case leads to a bond dissociation energy of (292 ± 5) kJ·mol^{-1} for sulfolane. Benson (1978) lists bond dissociation energies in the range 285 kJ·mol^{-1} to 293 kJ·mol^{-1} for aliphatic and aromatic sulfones. The decomposition temperatures noted in Table 1 for cyclohexanol (464 K), 2-cyclohexen-1-one (459 K), and (±)-2-ethylhexanoic acid (507 K) are all too low to signify radical formation being the initial step in the decomposition reactions. In each case a concerted condensation reaction mechanism (Benson, 1978) is the probable initial pathway.

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