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Vapor Pressure of Acetophenone, (±)-1,2-Butanediol, (±)-1,3-Butanediol, Diethylene Glycol Monopropyl Ether, 1,3-Dimethyladamantane, 2-Ethoxyethyl Acetate, Ethyl Octyl Sulfide, and Pentyl Acetate

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This paper reports measurements made within the DIPPR[‡] Project 821 for the 1992 Project Year. Vapor pressures were measured to a pressure limit of 270 kPa or lower decomposition point for eight compounds using an inclined-piston and twin ebulliometric apparatus. Liquid-phase densities along the saturation line were measured for each compound over a range of temperature (ambient to a maximum of 548 K). A differential scanning calorimeter (dsc) was used to measure two-phase (liquid + vapor) heat capacities for each compound in the temperature region ambient to the critical temperature or lower decomposition point. Where possible, the critical temperature and critical density for each compound were determined experimentally. The results of the measurements were combined to derive a series of thermophysical properties including critical temperature, critical density, critical pressure, acentric factor, enthalpies of vaporization [restricted to within ±50 K of the temperature region of the experimentally determined vapor pressures], 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 extended corresponding states. 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. The temperature at which initiation of thermal decomposition by a bond scission reaction occurs is discussed. A “Rule-Of-Thumb” is derived to estimate thermal decomposition temperatures by radical scission from a knowledge of the bond dissociation energy or vice versa. Compounds studied were acetophenone, (±)-1,2-butanediol, (±)-1,3-butanediol, diethylene glycol monopropyl ether, 1,3-dimethyladamantane, 2-ethoxyethyl acetate, ethyl octyl sulfide, and pentyl acetate.

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 compounds 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 to correlate 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 mol %) each of the compounds chosen for vapor-pressure studies; to measure the vapor pressure of each sample in the pressure regions 2 to 270 kPa or from the triple point to the decomposition temperature, if the corresponding pressure is less than 270 kPa; to use the dsc method developed at NIPER to experimentally measure two-phase (liquid + vapor) heat capacities for each compound in the temperature region ambient to the critical temperature or lower decomposition point; to determine, if possible, the critical temperature and critical density for each compound; to determine liquid-phase densities along the saturation line over a wide temperature range (up to 548 K if possible) for each compound; to fit the measured vapor pressures to a Wagner form vapor-pressure equation {the Wagner (1973) equation in the formulation given by Ambrose and Walton (1989)

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

where $T_r = T/T_c$ and $Y = (1 - T_r)$, was used}; to use fitting procedures to determine heat capacities along the saturation line and derive the critical pressure; to derive an acentric factor for each compound; to derive enthalpies of vaporization for each compound, using the Clapeyron equation (extrapolations are restricted to within ±50 K of the temperature region of the experimentally determined vapor pressures); and to derive the solubility parameter for each compound. The solubility parameter is defined as $\delta = [(\Delta_l^g H_m - RT)\rho]^{1/2}$ where $\Delta_l^g H_m$ is the enthalpy of vaporization at 298.15 K, R is the gas constant, $T = 298.15$ K, and ρ is the saturation liquid density at 298.15 K.

For over 40 years this laboratory has been at the forefront of technical development in the accurate and precise measurement of vapor pressures of pure compounds in the pressure range 0.01 kPa to 270 kPa and temperature range 100 K to 675 K. Details of the equipment used and recent innovations to extend the temperature range from 450 K to the present 675 K limit are given (Swietoslawski, 1945; Osborn and Douslin, 1966; Chirico et al., 1989b; Douslin and McCullough, 1963; Douslin and Osborn, 1965;

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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
Acetophenone											
d	360.458	2.0000	0.0001	0.0001	0.044	w	446.382	47.375	−0.001	0.002	0.011
d	375.764	3.9999	−0.0003	0.0003	0.027	w	453.536	57.817	−0.001	0.003	0.012
d	382.589	5.3330	−0.0003	0.0003	0.022	w	460.736	70.120	−0.004	0.003	0.011
d	392.737	7.9989	−0.0003	0.0005	0.018	w	467.976	84.533	−0.002	0.004	0.011
d	400.347	10.666	0.000	0.001	0.016	w	475.260	101.325	−0.001	0.004	0.011
d	406.499	13.332	0.000	0.001	0.014	w	482.587	120.79	0.00	0.01	0.012
d	412.887	16.665	0.001	0.001	0.013	w	489.960	143.25	0.00	0.01	0.013
d	418.193	19.933	0.001	0.001	0.013	w	497.373	169.02	0.00	0.01	0.015
d	425.176	25.023	0.000	0.001	0.012	w	504.831	198.49	0.00	0.01	0.016
w	425.174[b]	25.023	0.002	0.001	0.013	w	512.329	232.02	0.00	0.01	0.018
w	432.203	31.177	−0.001	0.002	0.012	w	519.866	270.02	0.00	0.01	0.021
w	439.271	38.565	0.000	0.002	0.012	w					
(±)-1,2-Butanediol											
d	372.553	2.0000	0.0003	0.0001	0.027	w	439.619	31.177	0.004	0.002	0.007
d	376.969	0.0003	0.0001	0.027	0.027	w	445.563	38.565	0.003	0.002	0.006
d	385.785	2.5389	0.0004	0.0002	0.016	w	451.529	47.375	0.001	0.003	0.007
d	391.650	3.9999	−0.0006	0.0003	0.014	w	457.519	57.817	0.001	0.003	0.007
d	400.329	5.3330	−0.0011	0.0003	0.012	w	463.536	70.120	0.000	0.004	0.008
d	406.809	7.9989	−0.0012	0.0005	0.010	w	469.575	101.325	−0.007	0.005	0.008
d	412.031	10.6661	−0.0009	0.0006	0.009	w	475.641	120.79	−0.01	0.01	0.008
d	417.436	13.332	−0.001	0.001	0.008	w	481.736	143.25	−0.01	0.01	0.009
d	421.914	16.665	0.001	0.001	0.008	w	487.855	169.02	−0.01	0.01	0.009
d	427.794	19.933	0.003	0.001	0.007	w	494.005	198.49	−0.01	0.01	0.009
w	427.794[b]	25.023	0.004	0.001	0.007	w	500.180	232.02	0.01	0.01	0.010
w	433.696	25.023	0.004	0.002	0.007	w	506.385	270.02	0.03	0.01	0.011
(±)-1,3-Butanediol											
ip.	364.978	0.6902	0.0009	0.0003		w	439.392[b]	25.023	0.008	0.002	0.011
ip.	369.976	0.9308	−0.0004	0.0003		w	445.334	31.177	0.008	0.002	0.009
ip.	374.972	1.2521	0.0069	0.0004		w	451.293	38.565	0.008	0.002	0.009
ip.	384.978[b]	2.1828	0.0184	0.0005		w	457.269	47.375	0.006	0.003	0.009
d	383.502	2.0000	0.0004	0.0001	0.036	w	463.265	57.817	0.002	0.003	0.009
d	388.934	2.6660	−0.0002	0.0002	0.028	w	469.281	70.120	−0.003	0.004	0.008
d	396.948	3.9999	−0.0016	0.0003	0.021	w	475.319	84.533	−0.010	0.004	0.008
d	402.892	5.3330	−0.0020	0.0003	0.019	w	481.380	101.325	−0.020	0.005	0.008
d	411.676	7.9989	−0.0015	0.0005	0.016	w	487.464	120.79	−0.03	0.01	0.009
d	418.226	10.6661	−0.0005	0.0006	0.014	w	493.575	143.25	−0.04	0.01	0.008
d	423.498	13.332	0.001	0.001	0.012	w	499.706	169.02	−0.03	0.01	0.008
d	428.953	16.665	0.003	0.001	0.012	w	505.869	198.49	−0.02	0.01	0.008
d	433.470	19.933	0.004	0.001	0.010	w	512.054	232.02	0.02	0.01	0.008
d	439.393	25.023	0.007	0.001	0.010	w	518.265[b]	270.02	0.10	0.01	0.008
Diethylene Glycol Monopropyl Ether											
d	377.664	2.0000	0.0008	0.0001	0.142	w	439.926[b]	25.023	0.007	0.001	0.062
d	392.440	3.9999	−0.0011	0.0003	0.106	w	446.677	31.177	−0.001	0.002	0.057
d	399.026	5.3330	−0.0042	0.0003	0.095	w	453.456	38.565	0.003	0.002	0.049
d	408.781	7.9989	−0.0028	0.0005	0.091	w	460.288	47.375	−0.010	0.002	0.045
d	416.089	10.6661	0.0002	0.0006	0.083	w	467.157	57.817	−0.020	0.003	0.039
d	421.993	13.332	0.004	0.001	0.077	w	474.063	70.120	−0.024	0.003	0.037
d	428.128	16.665	0.005	0.001	0.075	w	481.007	84.533	−0.019	0.004	0.037
d	433.223	19.933	0.006	0.001	0.073	w	487.985	101.325	0.008	0.004	0.041
d	439.936	25.023	−0.002	0.001	0.059	w	495.006	120.79	0.04	0.01	0.044
1,3-Dimethyladamantane											
d	352.168	2.0000	0.0002	0.0001	0.038	w	436.851	38.565	0.000	0.002	0.010
d	358.690	2.6660	−0.0003	0.0002	0.035	w	444.628	47.375	0.000	0.002	0.010
d	368.390	3.9999	0.0001	0.0002	0.024	w	452.477	57.817	−0.003	0.003	0.009
d	375.661	5.3330	−0.0002	0.0003	0.020	w	460.393	70.120	−0.002	0.003	0.010
d	386.509	7.9989	−0.0002	0.0004	0.015	w	468.379	84.533	−0.001	0.004	0.011
d	394.676	10.6661	−0.0003	0.0006	0.014	w	476.435	101.325	−0.003	0.004	0.011
d	401.296	13.332	0.000	0.001	0.013	w	484.560	120.79	0.00	0.00	0.010
d	408.190	16.665	0.000	0.001	0.012	w	492.756	143.25	0.00	0.01	0.012
d	413.928	19.933	0.001	0.001	0.011	w	501.014	169.02	0.01	0.01	0.013
d	421.499	25.023	0.001	0.001	0.011	w	509.347	198.49	0.01	0.01	0.013
w	421.497[b]	25.023	0.003	0.001	0.011	w	517.744	232.02	0.01	0.01	0.015
w	429.141	31.177	0.001	0.002	0.010	w	526.208	270.02	−0.01	0.01	0.015
2-Ethoxyethyl Acetate											
d	330.003	2.0000	0.0002	0.0001	0.027	w	398.389	38.565	0.000	0.002	0.011
d	335.343	2.6660	−0.0003	0.0002	0.020	w	404.577	47.375	−0.001	0.003	0.011
d	343.261	3.9999	−0.0001	0.0003	0.018	w	410.807	57.817	−0.002	0.003	0.011
d	349.177	5.3330	−0.0004	0.0003	0.015	w	417.078	70.120	−0.002	0.003	0.011
d	357.973	7.9989	0.0001	0.0005	0.014	w	423.390	84.533	−0.001	0.004	0.011
d	364.574	10.6661	0.0003	0.0006	0.012	w	429.744	101.325	−0.003	0.005	0.010
d	369.912	13.332	0.001	0.001	0.012	w	436.137	120.79	0.00	0.01	0.011
d	375.459	16.665	0.000	0.001	0.011	w	442.574	143.25	0.00	0.01	0.011
d	380.067	19.933	0.000	0.001	0.011	w	449.047	169.02	0.01	0.01	0.012
d	386.133	25.023	0.000	0.001	0.010	w	455.564	198.49	0.00	0.01	0.013
w	386.130[b]	25.023	0.003	0.001	0.011	w	462.119	232.02	−0.01	0.01	0.014
w	392.240	31.177	0.001	0.002	0.011	w	468.714	270.02	−0.04	0.01	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
Ethyl Octyl Sulfide											
d	384.753	2.0000	0.0004	0.0001	0.041	w	467.428	38.565	0.003	0.002	0.008
d	391.181	2.6660	−0.0002	0.0002	0.028	w	474.943	47.375	0.002	0.002	0.008
d	407.859	5.3330	−0.0007	0.0003	0.017	w	482.512	57.817	0.001	0.003	0.008
d	418.481	7.9989	−0.0008	0.0004	0.016	w	490.134	70.120	0.002	0.003	0.009
d	426.459	10.6661	−0.0006	0.0006	0.012	w	497.813	84.533	−0.004	0.004	0.008
d	432.916	13.332	0.000	0.001	0.011	w	505.543	101.325	−0.009	0.004	0.009
d	439.628	16.665	0.000	0.001	0.010	w	513.322	120.79	−0.01	0.01	0.010
d	445.208	19.933	0.001	0.001	0.009	w	521.158	143.25	−0.01	0.01	0.010
d	452.558	25.023	0.003	0.001	0.010	w	529.038	169.02	−0.02	0.01	0.012
w	452.557[b]	25.023	0.004	0.001	0.008	w	536.962	198.49	0.01	0.01	0.016
w	459.996	31.177	−0.023	0.002	0.009	w	544.933	232.02	0.03	0.01	0.021
Pentyl Acetate											
d	321.369	2.0000	−0.0002	0.0001	0.020	w	396.984	47.375	0.000	0.002	0.007
d	334.757	3.9999	0.0014	0.0003	0.018	w	403.320	57.817	0.000	0.003	0.007
d	340.753	5.3330	−0.0007	0.0003	0.016	w	409.700	70.120	0.002	0.003	0.009
d	349.664	7.9989	−0.0009	0.0005	0.012	w	416.126	84.533	0.001	0.004	0.008
d	356.355	10.6661	−0.0006	0.0006	0.011	w	422.595	101.325	0.001	0.005	0.008
d	361.769	13.332	0.000	0.001	0.010	w	429.109	120.79	0.00	0.01	0.009
d	367.396	16.665	0.001	0.001	0.009	w	435.668	143.25	0.00	0.01	0.009
d	372.075	19.933	0.000	0.001	0.008	w	442.269	169.02	0.00	0.01	0.009
d	378.235	25.023	0.002	0.001	0.008	w	448.915	198.49	0.00	0.01	0.009
w	378.239[b]	25.023	−0.002	0.001	0.007	w	455.604	232.02	0.00	0.01	0.010
w	384.444	31.177	−0.002	0.002	0.006	w	462.334	270.02	0.00	0.01	0.009
w	390.693	38.565	−0.002	0.002	0.007						

[a] Water (w) or decane (d) 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. Δp is the difference of the value of pressure, calculated with eq 1 and the parameters listed in Table 5, from the observed value of pressure ($\Delta p = p - p_{\mathrm{Wagner}}$). σ is the propagated error calculated using $\sigma(p) = 1.5 \times 10^{-4}p + 0.2$ Pa (inclined piston) or $\sigma(p) = (0.001)\,\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_{\mathrm{x}}/\mathrm{d}T)^2\}^{1/2}$ (ebulliometer). ΔT is the difference between the boiling and condensation temperatures ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the sample. [b] Point excluded from Wagner equation fit.

Steele et al., 1988a). In the pressure range 0.01 kPa to 3.5 kPa an inclined-piston gauge is used to make the vapor-pressure measurements. Twin ebulliometers are used in the pressure range 2 kPa to 270 kPa. The overlap region provides a check of the consistency of the methods. This is necessary in accurate and precise work since the inclined-piston is a static apparatus and, hence, the results are susceptible to the presence of dissolved gases in the sample.

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

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

Using a dsc technique developed at NIPER and accurate vapor pressures in the region below 270 kPa, it has been shown (Steele et al., 1988a; Knipmeyer et al., 1989; Chirico et al., 1989a) that reliable critical pressures can be derived. At NIPER, one of the objectives of the research programs funded by the U.S. Department of Energy is the extension of temperature limits of the in-house apparatus. In the area of heat capacity measurements, this objective has been fulfilled by the development of the dsc technique [applicable to 950 K (see Steele, 1995)] to measure heat capacities to within 20 K of the critical point (Steele et al., 1988b; Knipmeyer et al., 1989). Combination of the measured two-phase (liquid + vapor) heat capacities (obtained for a minimum of three cell fillings) and vapor-pressure data (measured within the inclined-piston and ebulliometric regions) has enabled estimation of the critical pressure for the substance under study. The fitting procedures used have been described (Steele et al., 1988b; Knipmeyer et al., 1989; Steele, 1995). In addition, where sample decomposition does not occur or is sufficiently slow, the dsc has been used to obtain the critical temperature and critical density by mapping the two-phase (liquid + vapor) to one-phase (fluid) conversion region.

Derivation of heat capacities along the saturation line requires an accurate knowledge of the liquid-phase density. Hence, a vibrating-tube densitometer capable of measurements from ambient to 548 K (the temperature limit of both used in the measurements) has been 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 lists the structural formulas, names, and Chemical Abstracts Service registry numbers (CAS No.) for each of the compounds studied in the 1992 project year for Project 821. Common synonyms are listed for each compound name.

Experimental Section

The apparatus and procedures used in obtaining the experimental data have been previously described in the

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

T/K	$C^{\rm II}_{\rm X,m}/R$	$C^{\rm II}_{\rm X,m}/R$	$C^{\rm II}_{\rm X,m}/R$	T/K	$C^{\rm II}_{\rm X,m}/R$	$C^{\rm II}_{\rm X,m}/R$	$C^{\rm II}_{\rm X,m}/R$
			Acetophenone				
mass/g	0.012 719	0.016 193	0.024 753	mass/g	0.012 719	0.016 193	0.024 753
vol cell/cm^3	0.053 39	0.052 72	0.053 39	vol cell/cm^3	0.053 39	0.052 72	0.053 39
315.0	26.4	25.1	25.4	535.0	36.6	35.5	34.7
335.0	26.0	26.3	26.0	555.0	37.7	36.7	35.7
355.0	26.4	26.7	26.7	575.0	39.1	37.7	36.3
375.0	28.2	27.2	27.6	595.0	39.8	38.7	37.1
395.0	28.2	28.4	28.4	615.0	41.2	39.3	38.2
415.0	29.7	29.4	29.3	635.0	43.4	40.7	39.3
435.0	30.7	30.3	30.2	655.0	45.2	42.1	40.5
455.0	31.8	31.4	31.0	675.0		43.9	41.8
475.0	33.0	32.4	31.9	695.0		49.2	42.4
495.0	34.1	33.3	32.8	715.0^b		42.2	32.1
515.0	35.2	34.3	33.6				
			(±)-1,2-Butanediol				
mass/g	0.010 233	0.015 969	0.023 497	mass/g	0.010 233	0.015 969	0.023 497
vol cell/cm^3	0.053 39	0.053 39	0.052 72	vol cell/cm^3	0.053 39	0.053 39	0.052 72
315.0	29.1	29.0	28.8	495.0	39.0	38.2	37.9
335.0	30.7	30.7	30.7	515.0	40.2	39.2	38.7
355.0	31.5	31.9	32.2	535.0	41.4	39.8	39.1
375.0	32.6	33.0	33.0	555.0	42.8	40.6	39.6
395.0	33.3	34.1	33.8	575.0	44.4	41.6	40.1
415.0	34.4	34.9	35.0	595.0	46.3	42.3	40.9
435.0	35.8	35.7	35.9	615.0	49.3		
455.0	36.7	36.5	36.7	635.0^b	50.5		
475.0	37.4	37.2	37.2				
			(±)-1,3-Butanediol				
mass/g	0.011 124	0.015 061	0.021 086	mass/g	0.011 124	0.015 061	0.021 086
vol cell/cm^3	0.053 39	0.052 72	0.053 39	vol cell/cm^3	0.053 39	0.052 72	0.053 39
315.0		26.7	27.4	495.0	39.2	38.9	37.7
335.0	28.4	28.4	28.4	515.0	40.3	39.6	38.5
355.0	30.2	30.3	30.4	535.0	41.4	40.6	39.1
375.0	32.4	32.5	32.1	555.0	42.7	41.3	39.6
395.0	33.5	33.9	33.3	575.0	43.9	42.3	40.1
415.0	34.9	35.0	34.6	595.0	45.2	43.5	40.5
435.0	36.1	36.1	35.5	615.0	45.9	44.3	40.8
455.0	37.0	37.1	36.4	635.0		45.8	
475.0	38.2	38.1	37.1				
			Diethylene Glycol Monopropyl Ether				
mass/g	0.010 568	0.015 950	0.021 489	mass/g	0.010 568	0.015 950	0.021 489
vol cell/cm^3	0.053 39	0.053 39	0.053 39	vol cell/cm^3	0.053 39	0.053 39	0.053 39
315.0	40.1	39.8	40.3	455.0	48.0	48.0	48.3
335.0	41.3	41.0	41.3	475.0	49.1	49.3	49.4
355.0	42.1	42.5	42.9	495.0	50.6	50.1	50.4
375.0	43.5	43.9	43.9	515.0	52.1	51.3	51.5
395.0	44.4	45.0	45.0	535.0	53.6	52.2	52.3
415.0	45.5	46.1	46.2	555.0	55.1	53.6	53.1
435.0	47.0	47.1	47.3				
			1,3-Dimethyladamantane				
mass/g	0.009 099	0.015 216	0.020 705	mass/g	0.009 099	0.015 216	0.020 705
vol cel/cm^3	0.053 37	0.053 37	0.052 72	vol cel/cm^3	0.053 37	0.053 37	0.052 72
315.0	33.7	31.8	32.1	535.0	53.5	52.7	51.8
335.0	33.9	34.2	34.2	555.0	55.2	54.7	53.1
355.0	36.6	36.2	35.9	575.0	57.7	56.4	55.2
375.0	38.1	37.9	37.9	595.0	59.9	57.6	56.0
395.0	39.7	39.9	39.6	615.0	62.8	59.7	57.7
415.0	41.8	41.7	41.4	635.0	64.4	61.4	59.8
435.0	43.5	43.7	43.0	655.0	68.0	63.7	61.5
455.0	45.0	45.7	45.0	675.0	70.8	66.8	63.7
475.0	47.9	47.3	46.6	695.0	69.1	74.5	68.5
495.0	49.5	49.2	48.4	715.0^b		60.5	54.8
515.0	51.6	51.2	50.2				
			2-Ethoxyethyl Acetate				
mass/g	0.012 148	0.015 264	0.021 174	mass/g	0.012 148	0.015 264	0.021 174
vol cell/cm^3	0.053 39	0.053 39	0.052 72	vol cell/cm^3	0.053 39	0.053 39	0.052 72
315.0	33.6	32.0	31.9	495.0	42.5	41.7	40.4
335.0	32.3	33.3	32.3	515.0	43.7	44.0	41.6
355.0	34.1	33.6	33.9	535.0	45.7	43.9	42.7
375.0	34.6	34.5	35.4	555.0	47.8	45.8	44.2
395.0	35.7	35.3	35.3	575.0	50.7	48.4	46.2
415.0	36.7	36.2	36.0	595.0	57.0	54.5	50.6
435.0	38.0	37.7	37.2	615.0^b	41.7	42.9	34.7
455.0	39.1	38.8	38.1	635.0^b	36.3	36.2	35.3
475.0	40.7	40.3	39.1				

Table 2 (Continued)

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	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$
			Ethyl Octyl Sulfide				
mass/g	0.009 488	0.015 841	0.022 373	mass/g	0.009 488	0.015 841	0.022 373
vol cell/cm^3	0.052 72	0.052 72	0.053 39	vol cell/cm^3	0.052 72	0.052 72	0.053 39
315.0	42.4	42.0	42.0	475.0	54.6	54.1	53.5
335.0	43.1	43.5	43.3	495.0	55.8	55.4	54.9
355.0	44.7	44.8	44.7	515.0	58.0	57.5	56.3
375.0	46.0	46.1	46.0	535.0	60.2	58.6	57.5
395.0	47.9	47.8	47.8	555.0	61.0	60.2	58.8
415.0	49.5	49.2	49.2	575.0	65.1	61.7	60.7
435.0	51.0	50.5	50.8	595.0[b]	66.7	60.1	59.1
455.0	53.0	52.3	52.3				
			Pentyl Acetate				
mass/g	0.010 849	0.015 957	0.020 585	mass/g	0.010 849	0.015 957	0.020 585
vol cell/cm^3	0.053 39	0.053 39	0.052 72	vol cell/cm^3	0.053 39	0.053 39	0.052 72
315.0	31.7	31.0	30.2	475.0	42.3	40.8	40.1
335.0	31.1	33.0	32.0	495.0	44.0	42.2	40.9
355.0	33.2	33.1	32.9	515.0	46.0	44.0	42.7
375.0	34.6	34.1	34.0	535.0	47.7	45.6	44.1
395.0	35.8	35.2	35.1	555.0	50.3	47.3	45.9
415.0	37.5	36.7	36.4	575.0	56.1	50.8	48.0
435.0	39.3	37.9	37.5	595.0[b]	55.6	53.4	43.8
455.0	40.3	39.4	38.7				

[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.

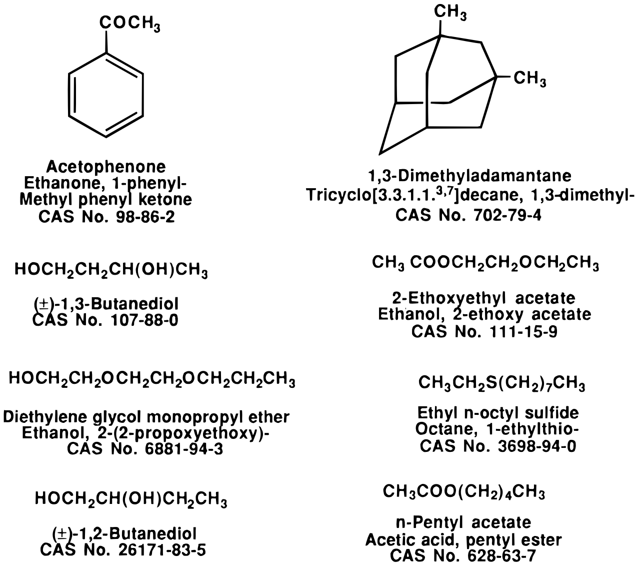

Figure 1. Structural formulas, common names, (Chemical Abstracts Service names, supplied by the authors), and Chemical Abstracts Services Registry Numbers (CAS No., supplied by the authors) for the compounds studied in this research.

literature and in various DOE reports. In addition, the preceding paper (Steele et al., 1996) gives 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. (1996) 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 except diethylene glycol monopropyl ether 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 sample of diethylene glycol monopropyl ether was supplied with a stated purity (by glc) of >99.90% by Eastman Chemicals Ltd. 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 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 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, $R = 8.314\ 51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, adopted by CODATA (Cohen and Taylor, 1988). The platinum resistance thermometers used in these measurements were calibrated by comparison with standard 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 acetophenone, (±)-1,2-butanediol, (±)-1,3-butanediol, diethylene glycol monopropyl ether, 1,3-dimethyladamantane, 2-ethoxyethyl acetate, ethyl octyl sulfide, and pentyl acetate are listed in Table 1. Following previous practice (Osborn and Douslin, 1966; Chirico et al., 1989b), the results obtained in the ebulliometric measurements were adjusted to common pressures. The common pressures, the condensation temperatures, and the difference between the condensation and boiling temperatures for the samples are reported. The small differences between the boiling and condensation temperatures in the ebulliometric measurements indicated correct operation of the equipment and the high purity of the samples studied.

Inclined-piston vapor-pressure measurements for (±)-1,3-butanediol are also listed in Table 1. For this compound the inclined-piston values extend the range of measured values down to 320 K.

The difference between the boiling and condensation temperatures (ΔT) for ethyl octyl sulfide increased significantly above 545 K. An attempt was made to make a measurement at 270 kPa (552 K), but ΔT started at approximately 0.03 K and rapidly increased by several tenths of a degree. This phenomenon is normally indicative of sample decomposition. Sample decomposition was also noted in the dsc measurements above 585 K.

For diethylene glycol monopropyl ether, the difference between the boiling and condensation temperatures (ΔT) increased significantly above 496 K. An attempt was made to make a measurement at 143 kPa (502 K), but ΔT started at approximately 0.05 K and rapidly increased by several tenths of a degree. Again, sample decomposition was also noted in the dsc measurements above 555 K.

Differential Scanning Calorimetry. Table 2 lists the two-phase heat capacities $C^{\mathrm{II}}_{\mathrm{x,m}}$ determined by dsc for acetophenone, (±)-1,2-butanediol, (±)-1,3-butanediol, diethylene glycol monopropyl ether, 1,3-dimethyladamantane, 2-ethoxyethyl acetate, ethyl octyl sulfide, and pentyl acetate for the given cell fillings. Heat capacities were determined at 20 K intervals with a heating rate of 0.083 $\mathrm{K{\cdot}s^{-1}}$ and a 120 s equilibration period between heats. For each compound the upper temperature bound of the measurements was set by the critical region or earlier sample decomposition.

For diethylene glycol monopropyl ether and ethyl octyl sulfide extensive sample decomposition precluded attainment of heat-capacity measurements above the highest listed temperatures.

For acetophenone, (±)-1,2-butanediol, (±)-1,3-butanediol, 1,3-dimethyladamantane, 2-ethoxyethyl acetate, and pentyl acetate measurements in the critical region were possible. For each compound an abrupt decrease in the heat capacity associated with the conversion from the 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 $\mathrm{K{\cdot}s^{-1}}$. 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, the cell volume calculated with eq 6 of Steele et al. (1996), and the measured temperatures at which conversion to a single phase was observed.

Critical temperatures and critical densities were derived graphically for acetophenone, (±)-1,2-butanediol, (±)-1,3-butanediol, 1,3-dimethyladamantane, 2-ethoxyethyl acetate, and pentyl acetate with these results, as seen in Figure 2. Results of measurements on benzene and toluene performed as "proof-of-concept measurements" for these procedures have been reported (Knipmeyer et al., 1989). The rapid heating method was used previously for critical temperature and critical density determinations for 2-aminobiphenyl (Steele et al., 1991), dibenzothiophene (Chirico et al., 1991), carbazole, phenanthrene, and benzofuran (Steele, 1995).

Densitometry. Measured densities for acetophenone, (±)-1,2-butanediol, (±)-1,3-butanediol, diethylene glycol monopropyl ether, 1,3-dimethyladamantane, 2-ethoxyethyl acetate, ethyl octyl sulfide, and pentyl acetate in the liquid phase along the saturation line are listed in Table 4. The temperatures are precise to ±0.005 K. The expected accuracy of the measured densities is ±0.1 $\mathrm{kg{\cdot}m^{-3}}$.

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
Acetophenone			
133.3	689.9	371.8	710.0
232.3	708.1	453.7	701.8
300.3	712.7		
(±)-1,2-Butanediol			
119.0	648.8	284.1	676.8
188.1	665.6	389.0	677.7
257.4	677.7		
(±)-1,3-Butanediol			
110.4	668.1	316.0	675.4
175.0	672.9	348.9	674.5
198.6	674.1	391.3	672.8
271.2	676.0		
1,3-Dimethyladamantane			
147.2	700.7	314.3	707.0
166.8	702.2	384.3	704.5
185.8	703.7	446.6	697.4
243.7	706.8		
2-Ethoxyethyl Acetate			
149.0	605.2	281.6	610.0
176.9	607.1	301.3	610.3
224.1	609.1	395.7	606.5
Pentyl Acetate			
161.6	594.3	290.9	600.0
200.2	599.0	347.1	599.3
259.4	600.1	384.9	594.3

Fitting Procedures. In general, the same fitting procedures were used for all eight compounds of this study. However, the number of fitting parameters differed depending on whether or not a critical temperature could be determined experimentally. For acetophenone, (±)-1,2-butanediol, (±)-1,3-butanediol, 1,3-dimethyladamantane, 2-ethoxyethyl acetate, and pentyl acetate critical temperatures were determined from the dsc measurements and, hence, only the critical pressure p_c was included in the variables. For diethylene glycol monopropyl ether and ethyl octyl sulfide extensive sample decomposition precluded critical temperature measurements and, therefore, both T_c and p_c were included as 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 $C^{\mathrm{II}}_{\mathrm{x,m}}$ given in Table 2. A summary of the procedure was outlined in Steele et al. (1996).

Derived Results. Table 5 listed the parameters derived using the procedures outlined above and in Steele et al. (1996). Details of the fits using the vapor-pressure results are given in Table 1 (column 4 labeled $\Delta p = p - p_{\mathrm{Wagner}}$ with p_{Wagner} calculated using the parameters listed in Table 5). Details of the fits of the measured liquid-phase densities to extended corresponding states using the parameters listed in Table 5 are given in column 3 of Table 4.

Values of $C^{\mathrm{II}}_{\mathrm{x,m}}(\rho = \rho_{\mathrm{sat}})$ were derived from the parameters listed in Table 5 and corresponding $C_{\mathrm{sat,m}}$ values were obtained using eq 6 of Steele et al. (1995). The results for $C_{\mathrm{sat,m}}/R$ are reported in Table 6. The estimated uncertainty in these values is 1%.

Enthalpies of vaporization $\Delta^{\mathrm{g}}_{\mathrm{l}}H_{\mathrm{m}}$ were derived from the Wagner-equation fits (Table 5) using the Clapeyron equation:

$$\mathrm{d}p/\mathrm{d}T = \Delta^{\mathrm{g}}_{\mathrm{l}}H_{\mathrm{m}}/(T\Delta^{\mathrm{g}}_{\mathrm{l}}V_{\mathrm{m}}) \qquad (2)$$

where $\Delta^{\mathrm{g}}_{\mathrm{l}}V_{\mathrm{m}}$ is the increase in molar volume from the liquid to the real vapor. Estimates of the liquid-phase volumes were made using eq 3, and the parameters are

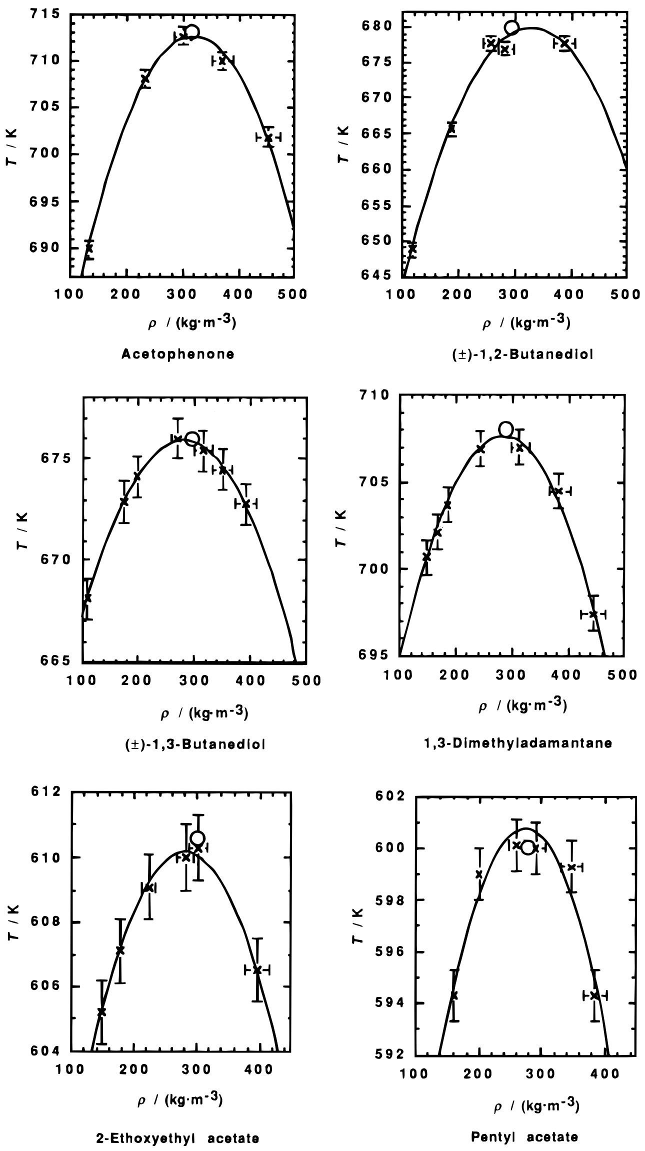

Figure 2. Vapor−liquid coexistence in the region of the critical point. ○ denotes the critical temperatures and critical densities derived in the fitting procedures. The curves are drawn as an aid to the eye and do not represent any theoretically valid equation. The crosses span the range of uncertainty.

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

T/K	ρ/kg·m^{-3}	$100(\rho - \rho_{c.s.})/\rho$
	Acetophenone	
323.136	1001.8	0.13
348.130	980.6	0.13
373.124	958.8	0.12
398.118	934.8	−0.05
423.113	910.8	−0.15
448.111	887.2	−0.13
473.111	863.2	−0.05
	(±)-1,2-Butanediol	
323.136	979.0	−0.61
348.137	959.8	−0.27
373.123	939.4	0.02
398.118	916.0	0.09
423.113	892.6	0.27
448.111	868.7	0.51
	(±)-1,3-Butanediol	
323.136	982.8	−0.93
348.130	965.1	−0.40
373.123	946.5	0.12
398.118	925.5	0.51
423.114	902.4	0.78
448.111	880.0	1.27
	Diethylene Glycol Monopropyl Ether	
323.136	938.0	0.08
348.130	918.7	0.24
373.123	896.0	0.19
398.118	871.4	−0.01
423.113	846.2	−0.18
448.111	821.6	−0.17
473.111	796.0	−0.14
	1,3-Dimethyladamantane	
323.136	880.4	−0.63
348.130	862.0	−0.57
373.122	844.0	−0.42
398.118	824.2	−0.40
423.113	804.8	−0.27
448.111	785.7	0.01
473.110	766.1	0.34
498.112	744.9	0.62
523.110	721.2	0.74
548.108	693.9	0.55
	2-Ethoxyethyl Acetate	
323.136	939.9	0.57
348.130	911.5	0.30
373.122	883.5	0.18
398.118	854.0	0.01
423.113	823.5	−0.12
448.111	791.9	−0.17
473.111	757.9	−0.24
498.108	719.4	−0.53
	Ethyl Octyl Sulfide	
323.136	817.5	0.49
348.137	798.8	0.38
373.123	779.7	0.28
398.118	758.6	−0.02
423.113	737.2	−0.28
448.111	716.1	−0.42
473.111	695.0	−0.44
	Pentyl Acetate	
323.136	846.5	0.20
348.130	822.3	0.18
373.124	797.2	0.18
398.118	769.8	0.03
423.113	740.7	−0.17
448.111	711.0	−0.22
473.111	679.5	−0.20

[a] $\rho_{c.s.}$ values were calculated using eq 3 and the parameters listed in Table 5.

given in Table 5. The estimates used a variation of the extended corresponding-states equation of Riedel (1955):

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

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. 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.

Table 5. Parameters for Eq 1 (This Paper) and Eq 9 of Steele et al. (1996), Critical Constants, and Acentric Factors[a]

	Acetophenone				(±)-1,2-Butanediol		
A	−8.938 60	b_0	−0.361 93	A	−9.986 62	b_0	−0.427 56
B	4.011 61	b_1	−0.962 17	B	5.098 69	b_1	−0.530 50
C	−4.594 10	b_2	1.939 28	C	−9.385 93	b_2	−0.930 70
D	−2.577 68	b_3	−2.137 40	D	−2.853 78	b_3	1.373 33
T_c	713 K	p_c	4400 kPa	T_c	680 K	p_c	5210 kPa
ρ_c	315.6 $\text{kg}\cdot\text{m}^{-3}$	ω	0.3991	ρ_c	297.4 $\text{kg}\cdot\text{m}^{-3}$	ω	0.6303
	(±)-1,3-Butanediol				Diethylene Glycol Monopropyl Ether		
A	−9.290 11	b_0	−0.442 73	A	−10.598 72	b_0	−0.601 66
B	3.031 08	b_1	−0.427 82	B	6.154 97	b_1	−0.838 59
C	−9.273 34	b_2	−1.613 02	C	−8.679 56	b_2	0.316 17
D	−1.053 46	b_3	2.752 73	D	−2.165 15	b_3	−0.617 01
T_c	676 K	p_c	4020 kPa	T_c	680 K	p_c	3040 kPa
ρ_c	294.8 $\text{kg}\cdot\text{m}^{-3}$	ω	0.7053	ρ_c	284.3 $\text{kg}\cdot\text{m}^{-3}$	ω	0.6139
	1,3-Dimethyladamantane				2-Ethoxyethyl Acetate		
A	−8.173 38	b_0	−0.666 71	A	−9.641 68	b_0	−0.481 98
B	3.288 72	b_1	−0.526 16	B	4.581 79	b_1	−0.962 47
C	−3.473 24	b_2	0.325 27	C	−6.259 93	b_2	1.445 69
D	−2.485 97	b_3		D	−4.120 66	b_3	−2.009 97
T_c	708 K	p_c	3000 kPa	T_c	610.6 K	p_c	3180 kPa
ρ_c	287.5 $\text{kg}\cdot\text{m}^{-3}$	ω	0.2960	ρ_c	299.6 $\text{kg}\cdot\text{m}^{-3}$	ω	0.5251
	Ethyl Octyl Sulfide				Pentyl Acetate		
A	−9.613 30			A	−8.097 53	b_0	−0.585 82
B	4.283 80			B	1.603 98	b_1	−0.187 04
C	−5.796 20			C	−3.374 06	b_2	−1.012 34
D	−3.969 75			D	−5.045 94	b_3	0.956 01
T_c	700 K	p_c	2400 kPa	T_c	600 K	p_c	2685 kPa
ρ_c	249.2 $\text{kg}\cdot\text{m}^{-3}$	ω	0.5358	ρ_c	277.4 $\text{kg}\cdot\text{m}^{-3}$	ω	0.4544

[a] The parameters listed in this table are those derived from the fitting procedures. Table 9 lists "recommended" critical parameters.

Solubility parameters are listed in Table 8. Table 9 lists "recommended" values for the critical properties for each of the eight compounds studied.

Discussion

General Comments. In this section emphasis is given to comparison of the measured properties of this research with experimentally determined values reported in the literature. Only passing references are made to correlated values available in the literature, mostly those abstracted in DIPPR Project 801 (Daubert and Danner, 1991).

The experimentally determined values for the critical densities (obtained via the dsc method) have a relatively large uncertainty attached (±2.5%). In all cases studied in this research, this range enclosed the value derived in fitting the density measurements to extended corresponding states.

Comparison with Literature Values. Acetophenone. Vapor-pressure measurements for acetophenone were reported by Kahlbaum (1898) and Ham et al. (1918), in the compilation of Stull (1947), and by Wilding et al. (1991) and Zhongxiu et al. (1991). Their results are compared in Figure 3. The results due to Kahlbaum are remarkably consistent with those obtained in this research with all reported values lying in a ±1% band except the reported value at 338 K which may be a typographical error. It is worth noting that at temperatures below 370 K the compiled values of Stull diverge in the direction opposite to the measured values of Ham et al. The recent vapor pressure measurements (Wilding et al., 1991; Zhongxiu et al., 1991) were obtained during VLE studies. In both cases the measured results are in poor agreement (see Figure 3) with those obtained using the Wagner vapor-pressure equation and the parameters listed in Table 5.

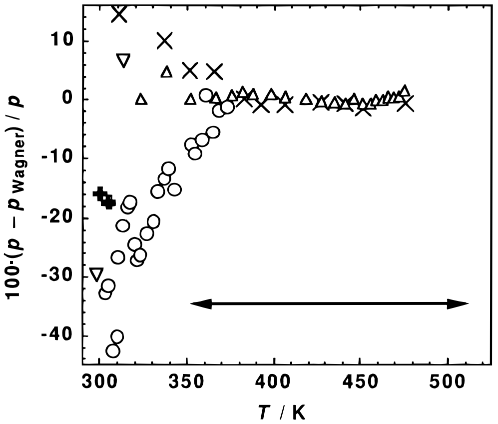

Figure 3. Comparison of literature vapor pressures for acetophenone with those obtained from the Wagner equation and the parameters listed in Table 5. The double-headed arrow represents the range of the measurements reported in Table 1. Key: (△) Kahlbaum (1898); (○) Ham et al. (1918); (×) Stull (1947); (▽) Wilding et al. (1991); (+) Zhongxiu et al. (1991).

Figure 4A compares values for the density of acetophenone found in a literature search (Perkins, 1896; Dutiot and Freinderich, 1900; Timmermans and Hennaut-Roland, 1935; Friend and Hargreaves, 1944; Lutskil, 1954) with values calculated using extended corresponding states, eq 3, and the parameters listed in Table 5. Note that both Perkins and Timmermanns and Hennaut-Roland list densities for the supercooled liquid (mp ~293 K). The equation derived by the DIPPR 801 Project compilers (Daubert and Danner, 1991) for the liquid-phase density of acetophenone gives values above 400 K, which are highly divergent from those reported in this research. It would appear that too much weight was attached to the measurements of both Perkins and Timmermanns and Hennaut-Roland in the derivation of the correlating equation for the DIPPR 801 Project.

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	$C_{\mathrm{sat,m}}/R$
	Acetophenone		
300.0	24.7	520.0	33.5
320.0	25.4	540.0	34.3
340.0	26.2	560.0	35.1
360.0	27.0	580.0	35.9
380.0	27.7	600.0	36.7
400.0	28.5	620.0	37.5
420.0	29.3	640.0	38.4
440.0	30.2	660.0	39.9
460.0	31.0	680.0	42.7
480.0	31.8	700.0	52.2
500.0	32.7		
	(±)-1,2-Butanediol		
300.0	28.0	500.0	37.4
320.0	29.5	520.0	37.8
340.0	30.8	540.0	38.2
360.0	32.1	560.0	38.6
380.0	33.2	580.0	39.2
400.0	34.1	600.0	40.0
420.0	35.0	620.0	41.3
440.0	35.7	640.0	44.0
460.0	36.3	660.0	51.0
480.0	36.9	670.0	62.2
	(±)-1,3-Butanediol		
300.0	25.5	500.0	37.7
320.0	27.5	520.0	38.1
340.0	29.3	540.0	38.4
360.0	30.9	560.0	38.8
380.0	32.4	580.0	39.2
400.0	33.7	600.0	39.8
420.0	34.8	620.0	40.8
440.0	35.7	640.0	42.9
460.0	36.5	660.0	49.1
480.0	37.1	670.0	62.7
	Diethylene Glycol Monopropyl Ether		
300.0	38.9	440.0	47.1
320.0	40.4	460.0	48.0
340.0	41.7	480.0	48.8
360.0	42.9	500.0	49.7
380.0	44.1	520.0	50.5
400.0	45.1	540.0	51.2
420.0	46.1		
	1,3-Dimethyladamantane		
300.0	30.5	520.0	49.8
320.0	32.5	540.0	51.3
340.0	34.5	560.0	52.8
360.0	36.4	580.0	54.2
380.0	38.3	600.0	55.8
400.0	40.1	620.0	57.4
420.0	41.8	640.0	59.4
440.0	43.5	660.0	62.0
460.0	45.2	680.0	66.5
480.0	46.8	700.0	82.4
500.0	48.3		
	2-Ethoxyethyl Acetate		
300.0	31.4	460.0	37.7
320.0	32.2	480.0	38.5
340.0	33.0	500.0	39.3
360.0	33.7	520.0	40.2
380.0	34.5	540.0	41.3
400.0	35.3	560.0	43.0
420.0	36.1	580.0	46.3
440.0	36.9	600.0	58.6
	Ethyl Octyl Sulfide		
300.0	41.0	460.0	52.2
320.0	42.4	480.0	53.6
340.0	43.8	500.0	55.0
360.0	45.2	520.0	56.4
380.0	46.6	540.0	57.8
400.0	48.0	560.0	59.2
420.0	49.4	580.0	60.6
440.0	50.8	600.0	62.0
	Pentyl Acetate		
300.0	29.3	460.0	38.3
320.0	30.7	480.0	39.4
340.0	31.9	500.0	40.7
360.0	33.1	520.0	42.1
380.0	34.2	540.0	43.9
400.0	35.2	560.0	46.4
420.0	36.3	580.0	51.4
440.0	37.3		

Table 7. Enthalpies of Vaporization Obtained from the Wagner and Clapeyron Equations[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}
	Acetophenone		
298.15^b	55.40 ± 0.43	440.0	46.31 ± 0.32
300.0^b	55.27 ± 0.43	460.0	44.99 ± 0.37
320.0^b	53.94 ± 0.40	480.0	43.63 ± 0.43
340.0^b	52.63 ± 0.37	500.0	42.19 ± 0.53
360.0	51.36 ± 0.35	520.0	40.68 ± 0.67
380.0	50.10 ± 0.32	540.0^b	39.09 ± 0.81
400.0	48.85 ± 0.30	560.0^b	37.40 ± 1.00
420.0	47.59 ± 0.30	580.0^b	35.59 ± 1.20
	(±)-1,2-Butanediol		
298.15^b	71.55 ± 0.80	440.0	55.64 ± 0.43
300.0^b	71.35 ± 0.78	460.0	53.28 ± 0.47
320.0^b	69.07 ± 0.72	480.0	50.82 ± 0.53
340.0^b	66.82 ± 0.65	500.0	48.26 ± 0.67
360.0^b	64.59 ± 0.58	520.0^b	45.57 ± 0.83
380.0	62.38 ± 0.53	540.0^b	42.78 ± 1.05
400.0	60.16 ± 0.48	560.0^b	39.87 ± 1.30
420.0	57.93 ± 0.45		
	(±)-1,3-Butanediol		
298.15^b	74.46 ± 1.01	440.0	59.54 ± 0.50
300.0^b	74.27 ± 1.00	460.0	57.06 ± 0.52
320.0	72.30 ± 0.81	480.0	54.40 ± 0.57
340.0	70.30 ± 0.73	500.0	51.54 ± 0.70
360.0	68.27 ± 0.67	520.0	48.47 ± 0.90
380.0	66.20 ± 0.62	540.0^b	45.17 ± 1.13
400.0	64.07 ± 0.57	560.0^b	41.67 ± 1.41
420.0	61.87 ± 0.52	580.0^b	37.79 ± 1.73
	Diethylene Glycol Monopropyl Ether		
298.15^b	65.71 ± 0.83	440.0	52.51 ± 0.40
300.0^b	65.53 ± 0.80	460.0	50.55 ± 0.43
320.0^b	63.66 ± 0.63	480.0	48.52 ± 0.52
340.0^b	61.79 ± 0.55	500.0	46.41 ± 0.63
360.0^b	59.95 ± 0.50	520.0^b	44.22 ± 0.80
380.0	58.11 ± 0.45	540.0^b	41.92 ± 1.00
400.0	56.27 ± 0.42	560.0^b	39.52 ± 1.25
420.0	54.41 ± 0.40		
	1,3-Dimethyladamantane		
298.15^b	49.37 ± 0.33	440.0	41.50 ± 0.32
300.0^b	49.26 ± 0.33	460.0	40.32 ± 0.37
320.0^b	48.12 ± 0.32	480.0	39.09 ± 0.45
340.0^b	47.00 ± 0.28	500.0	37.79 ± 0.57
360.0	45.91 ± 0.27	520.0	36.42 ± 0.70
380.0	44.82 ± 0.27	540.0^b	34.96 ± 0.85
400.0	43.73 ± 0.27	560.0^b	33.41 ± 1.03
420.0	42.64 ± 0.27	580.0^b	31.74 ± 1.21
	2-Ethoxyethyl Acetate		
280.0^b	54.36 ± 0.48	400.0	43.47 ± 0.35
298.15^b	52.61 ± 0.43	420.0	41.65 ± 0.42
300.0^b	52.43 ± 0.43	440.0	39.77 ± 0.52
320.0^b	50.57 ± 0.38	460.0	37.81 ± 0.67
340.0	48.76 ± 0.35	480.0^b	35.74 ± 0.86
360.0	46.99 ± 0.33	500.0^b	33.53 ± 1.08
380.0	45.24 ± 0.32	520.0^b	31.16 ± 1.35
	Ethyl Octyl Sulfide		
298.15^b	63.86 ± 0.60	460.0	49.76 ± 0.40
300.0^b	63.69 ± 0.60	480.0	48.06 ± 0.47
320.0^b	61.79 ± 0.55	500.0	46.26 ± 0.57
340.0^b	59.96 ± 0.50	520.0	44.38 ± 0.70
360.0^b	58.18 ± 0.45	540.0	42.40 ± 0.88
380.0^b	56.47 ± 0.42	560.0^b	40.29 ± 1.08
400.0	54.79 ± 0.38	580.0^b	38.03 ± 1.33
420.0	53.13 ± 0.37	600.0^b	35.58 ± 1.61
440.0	51.47 ± 0.37		
	Pentyl Acetate		
280.0^b	50.15 ± 0.42	400.0	40.35 ± 0.37
298.15^b	48.56 ± 0.37	420.0	38.65 ± 0.45
300.0^b	48.40 ± 0.37	440.0	36.82 ± 0.60
320.0^b	46.74 ± 0.33	460.0	34.85 ± 0.76
340.0	45.13 ± 0.32	480.0^b	32.68 ± 0.98
360.0	43.55 ± 0.30	500.0^b	30.31 ± 1.21
380.0	41.97 ± 0.32	520.0^b	27.67 ± 1.48

[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.

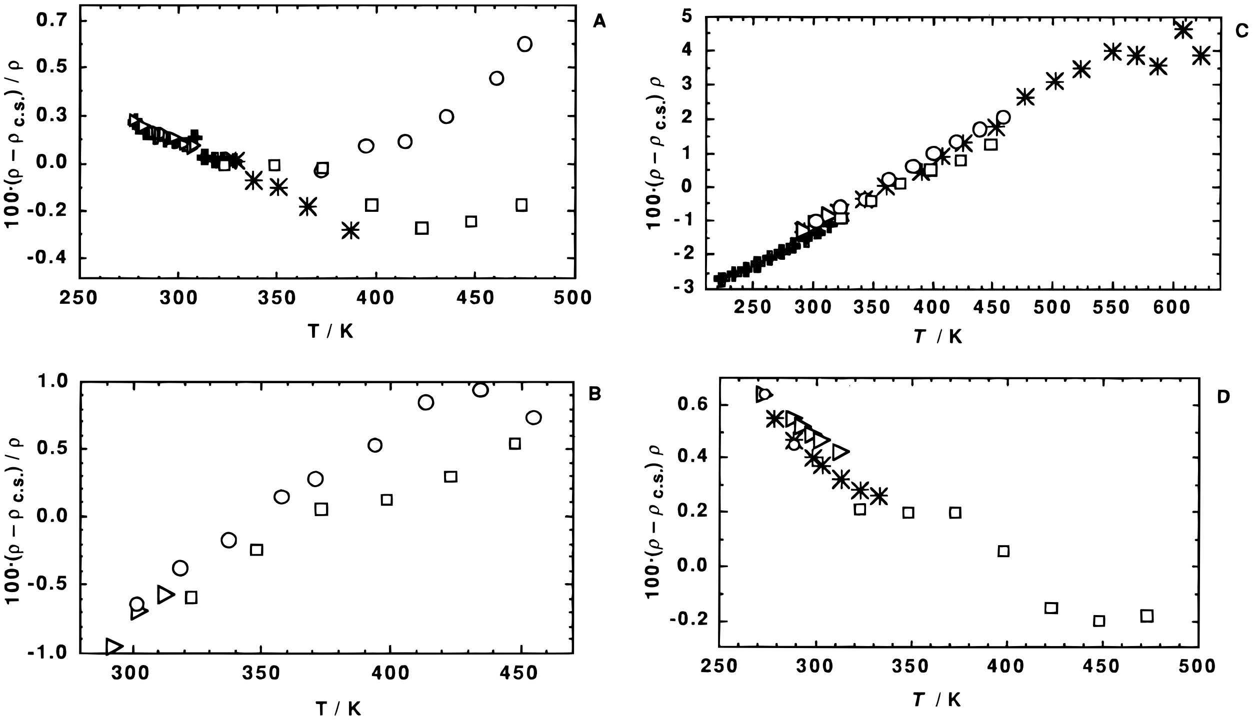

Figure 4. Comparison of literature density measurements with those obtained using extended corresponding states using eq 3 and the parameters listed in Table 5. (A) Acetophenone: (□) our research Table 4; (+) Perkins (1896); (*) Dutiot and Freinderich (1900); (△) Timmermans and Hennaut-Roland (1935); (○) Freind and Hargreaves (1944). (B) (±)-1,2-Butanediol: (□) our research Table 4; (△) Czechowski et al. (1988); (○) Sun et al. (1992). (C) (±)-1,3-Butanediol: (□) our research Table 4; (+) McDuffie et al. (1969); (*) Apaev et al. (1978); (△) Czechowski et al. (1988); (○) Sun et al. (1992). (D) Pentyl acetate: (□) our research Table 4; (○) Lievens (1924); (△) Timmermans and Hennaut-Roland (1955); (*) Karpushina et al. (1990).

Table 8. Solubility Parameters[a,b]

ρ/(mol·m^{-3})	$\Delta_l^g U_m$/J·mol^{-1}	δ/(J·m^{-3})$^{1/2}$
	Acetophenone	
8495.4	52 920	2.120×10^4
	(±)-1,2-Butanediol	
11037	69 070	2.761×10^4
	(±)-1,3-Butanediol	
11063	71 980	2.822×10^4
	Diethylene Glycol Monopropyl Ether	
6440.4	63 230	2.018×10^4
	1,3-Dimethyladamantane	
5486.6	46 890	1.604×10^4
	2-Ethoxyethyl Acetate	
7333.5	51 880	1.951×10^4
	Ethyl Octyl Sulfide	
4782.5	61 380	1.713×10^4
	Pentyl Acetate	
6667.6	47 670	1.783×10^4

[a] Densities (listed to an extra significant figure to prevent round off errors) were estimated by extrapolation of third-order fits of the values listed in Table 4. [b] $\Delta_l^g U_m = (\Delta_l^g H_m - RT)$ obtained using the value for the enthalpy of vaporization at 298.15 K listed in Table 7.

Table 9. "Recommended" Critical Properties[a]

compound	T_c/K	p_c/kPa	ρ_c/kg·m^{-3}
acetophenone	713 ± 1	4400 ± 100	316 ± 9
(±)-1,2-butanediol	680 ± 1	5210 ± 200	297 ± 9
(±)-1,3-butanediol	676 ± 1	4020 ± 200	295 ± 9
diethylene glycol monopropyl ether	680 ± 5	3040 ± 300	284 ± 15
1,3-dimethyladamantane	708 ± 1	3000 ± 200	288 ± 9
2-ethoxyethyl acetate	611 ± 1	3180 ± 100	300 ± 9
ethyl octyl sulfide	700 ± 10	2400 ± 300	249 ± 15
pentyl acetate	600 ± 1	2685 ± 100	277 ± 9

[a] Except for diethylene glycol monopropyl ether and ethyl octyl sulfide, the reported critical temperatures and critical densities and their allocated uncertainty intervals were obtained from the dsc measurements. For diethylene glycol monopropyl ether and ethyl octyl sulfide the critical temperatures are estimates. The critical pressures listed were determined using the fitting procedures detailed in the text.

Lutskil (1954) reported a density of 927 kg·m^{-3} for acetophenone at 404 K. In comparison a value of 930 kg·m^{-3} was interpolated from our results (Table 4).

A critical temperature of (713 ± 1) K and a critical density of (316 ± 9) kg·m^{-3} were obtained from our dsc measurements. Teja and Anselme (1990) observed corresponding values of (709.5 ± 0.4) K and (311 ± 6) kg·m^{-3} using a "rapid heating" sealed tube method. They noted that for both acetaldehyde and acetophenone the critical temperature increased with time and assumed association was occurring. In the case of acetaldehyde, the position of the appearance and disappearance of the meniscus moved down the tube with time, supporting their assumption of association. For acetophenone, they did not report any corresponding corroborating evidence. In a subsequent paper, Teja and Rosenthal (1991) reported a further study using both static and flow methods for the determination of critical properties. In that study they reported that acetophenone "exhibited a very slight *decrease* (our italics) in critical temperature and increase in critical pressure with residence time in the flow apparatus". Their apparatus "leaked and only a few data points could be obtained". Teja and Rosenthal (1991) obtained $T_c = (709.6 \pm 1.0)$ K and $p_c = (4010 \pm 50)$ kPa using the flow apparatus. In our research (NIPER) the fitting procedures gave a critical pressure for acetophenone of 4400 kPa (Table 5). Wilding et al. (1991) listed a critical temperature of 713 K and a critical pressure of 4060 kPa in a "table of data used in data reduction" as part of their VLE study mentioned above. However, they fail to give any sources for the values.

A search of the literature found only two single-temperature measurements of the saturated heat capacity of acetophenone (Phillip, 1939; Fuchs, 1980). Phillip obtained a value $C_{\mathrm{sat,m}}/R = 27.4$ at 303.15 K. Fuchs obtained values of $C_{\mathrm{sat,m}}/R = (24.61 \pm 0.04)$ and (24.72 ± 0.10) at 298.15 K. Interpolation and extrapolation of our results (Table 6) gave values for $C_{\mathrm{sat,m}}/R$ of (24.8 ± 0.2) at 303.15 K and (24.6 ± 0.2) at 298.15 K, respectively.

The DIPPR 801 correlation equation for enthalpies of vaporization of acetophenone is based on a value of $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ at 298.15 K listed in a compilation (Pedley et al., 1986). That value, $(55.9 \pm 1.3)\ \mathrm{kJ \cdot mol^{-1}}$, can be traced to an estimate made in Cox and Pilcher (1970) using an equation derived by Wadsö (1969) for slightly associating liquids, namely:

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}} = 20.9 + 0.1715[(T_{\mathrm{bp}}/\mathrm{K}) - 273] \quad (4)$$

Using eq 4 and the normal boiling point listed in Table 1 for acetophenone, a value $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K}) = 55.6\ \mathrm{kJ \cdot mol^{-1}}$ is obtained. In our research (Table 7), a value of $(55.40 \pm 0.43)\ \mathrm{kJ \cdot mol^{-1}}$ for $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ at 298.15 K was obtained.

(±)-1,2-Butanediol. A search of the literature failed to reveal any appreciable vapor-pressure measurements on 1,2-butanediol. Various handbooks list a vapor pressure of 10 mmHg (1.333 kPa) for a temperature of 369.6 K and a normal boiling point of 464.6 K. In this research the normal boiling point for (±)-1,2-butanediol was 469.575 K (Table 1). Using the parameters given in Table 5 and the (2.5, 5.0) form of the Wagner equation, the derived vapor pressure at 369.6 K was 12.7 mmHg (1.698 kPa).

Figure 4B compares values for the density of (±)-1,2-butanediol found in a literature search (Czechowski et al., 1988; Sun et al., 1992) with values calculated using extended corresponding states, eq 3, and the parameters listed in Table 5. Note that the difference $[(\rho - \rho_{\mathrm{c.s.}})/\rho_{\mathrm{c.s.}}]$ increases approximately linearly with temperature (see Table 4). A similar positive slope was shown (Joffe and Zudkevitch, 1974) for polar compounds. Joffe and Zudkevitch "corrected" for this slope by replacing the acentric factor in extended corresponding states, eq 3, by a linear function in temperature. It was noted in this research, that raising the critical temperature to 710 K and using an acentric factor of 0.6314 removed the positive slope.

(±)-1,3-Butanediol. Vapor pressures for (±)-1,3-butanediol have been reported (Schierholtz and Staples, 1935; Stull, 1947; Markovnik et al., 1987). Schierholtz and Staples list no actual results but give two equations to represent their results:

$$\log(p/\mathrm{mmHg}) = 9.3890 - 3116.7/(T/\mathrm{K}) \quad \text{in the range 373 K to 423 K}$$

and

$$\log(p/\mathrm{mmHg}) = 9.1979 - 3035.6/(T/\mathrm{K}) \quad \text{in the range 423 K to 480.5 K}$$

Results obtained using the former equation differ from values obtained using the Wagner equation and the parameters listed in Table 5 by 23% at 373 K, falling linearly to approximately 7% at 423 K. The latter equation, in contrast, gives values which are approximately 5% too high across the whole of its stated range of application.

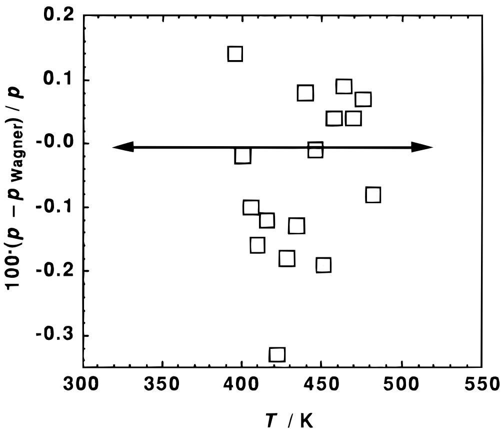

Figure 5. Comparison of literature vapor pressures for (±)-1,3-butanediol with those obtained using the Wagner equation and the parameters listed in Table 5. The double-headed arrow represents the range of the measurements reported in Table 1. Key: (□) Markovnik et al. (1987).

The vapor pressures listed by Stull are very different from those obtained in our research. At 295.43 K, Stull lists a pressure of 0.1333 kPa (1 mmHg) compared with our value of 0.0027 kPa obtained using the Wagner equation and the parameters listed in Table 5. This represents a difference of approximately 98%. At 479.65 K, Stull lists a pressure of 101.325 kPa (760 mmHg) compared with our value of 96.27 kPa. This represents a difference of approximately 5%. In the intervening region the difference between the values listed by Stull and our research is approximately linear in temperature.

In contrast to the above wide discrepancies, the results of Markovnik et al. are in excellent agreement with our values. Figure 5 compares the results listed by Markovnik et al. for (±)-1,3-butanediol with values obtained using the Wagner equation and the parameters listed in Table 5. Markovnik et al. state a sample purity of 99.9 mol %, comparable to that used in this research.

Figure 4C compares values for the density of (±)-1,3-butanediol found in a literature search (McDuffie et al., 1969; Apaev et al., 1978; Czechowski et al., 1988; Sun et al., 1992) with values calculated using extended corresponding states, eq 3, and the parameters listed in Table 5. Note the positive slope similar to that found for (±)-1,2-butanediol.

In order to compare the various densities over the temperature range 250 K to 500 K, the Apaev et al. densities were fit to a cubic equation in temperature and values were interpolated for each set of measurements and compared. The values obtained in our research (Table 4) were on average 0.2% lower than those interpolated from the results of Apaev et al. Values obtained by Sun et al. were 0.2% higher than the interpolation, whereas those by Czechowski et al. and McDuffie et al. where coincident with the interpolation.

Gardner and Hussain (1972), in a study of the standard enthalpies of formation of some aliphatic diols, report enthalpies of vaporization of (±)-1,3-butanediol based on the vapor pressure measurements (Schierholtz and Staples, 1935). The reported values $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(398\ \mathrm{K}) = 59.8\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K}) = (67.8 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$ can be compared with our values of $(64.1 \pm 0.6)\ \mathrm{kJ \cdot mol^{-1}}$ and $(74.46 \pm 1.01)\ \mathrm{kJ \cdot mol^{-1}}$ (Table 7).

Diethylene Glycol Monopropyl Ether. A critical temperature of (680 ± 5) K and a critical density of (284 ± 15) $\mathrm{kg \cdot m^{-3}}$ were obtained from the fitting procedures used in this research for diethylene glycol monopropyl ether.

Anselme and Teja (1990) observed corresponding values of (687 ± 13) K and (303 ± 5) kg·m^{-3} using a "rapid heating" sealed tube method. In a subsequent paper Teja and Rosenthal (1990) reported a further study using both static and flow methods for the determination of critical properties listing a critical temperature of (679.8 ± 1.0) K and a critical pressure of (3000 ± 20) kPa. In our research the derived critical pressure was (3040 ± 300) kPa. Since diethylene glycol monopropyl ether is unstable in the critical region, agreement between the various experimentally determined critical properties and the values derived from the fitting procedures can be considered as good.

1,3-Dimethyladamantane. The experimentally determined critical properties for 1,3-dimethyladamantane obtained in this research are the first reported for an adamantoid compound. An enthalpy of vaporization at 298.15 K derived from unpublished vapor-pressure measurements made by a "semi-micro ebulliometer" (Steele and Watt, 1977), $\Delta_{\rm l}^{\rm g}H_{\rm m}(298.15\ {\rm K}) = (67.8 \pm 1.3)$ kJ·mol^{-1}, is significantly different from that derived in this research, (49.37 ± 0.33) kJ·mol^{-1} (Table 7).

2-Ethoxyethyl Acetate. Kusano (1978) lists a normal boiling point of 429.3 K and a density of 967.61 kg·m^{-3} at 298.15 K for 2-ethoxyethyl acetate. The corresponding values obtained in this research are 429.74 K and 962.8 kg·m^{-3}, respectively.

A critical temperature of (610.6 ± 1.0) K and a critical density of (300 ± 6) kg·m^{-3} were obtained from the dsc measurements. Teja and Anselme (1990b) observed corresponding values of (608.7 ± 0.6) K and (298 ± 5) kg·m^{-3} using a "rapid heating" sealed tube method. In a subsequent paper Teja and Rosenthal (1990) reported a further study using both static and flow methods for the determination of critical properties and list a critical temperature of (607.3 ± 0.7) K and a critical pressure of (3166 ± 40) kPa. In our research the derived critical pressure was (3180 ± 100) kPa. Since 2-ethoxyethyl acetate is relatively unstable in the critical region, agreement between the various experimentally determined critical properties can be considered as good.

Kusano and Wadsö (1970) measured the enthalpy of vaporization at 298.15 K using a vaporization calorimeter. Their result $\Delta_{\rm l}^{\rm g}H_{\rm m}(298.15\ {\rm K}) = (52.67 \pm 0.08)$ kJ·mol^{-1} is in excellent agreement with the value of (52.61 ± 0.43) kJ·mol^{-1} obtained in this research (Table 7).

Ethyl Octyl Sulfide. No thermophysical property measurements for ethyl octyl sulfide were found in a search of the literature from 1930 through June 1996.

Pentyl Acetate. Figure 6 compares literature values for the vapor pressure of pentyl acetate with values obtained using the Wagner equation and the parameters listed in Table 5. Both references and the corresponding sets of measured values were obtained in a communication from the Editor of this journal.

Figure 4D compares literature (Lievens, 1924; Timmermans and Hennaut-Roland, 1955; Karpushina et al., 1990) values for the density of pentyl acetate with those obtained in this research and values derived using extended corresponding states, eq 3, and the parameters listed in Table 5. Values attributed to Karpushina et al. were calculated using the equation listed by them as representing the density in the temperature interval 278.15 K to 333.15 K for pentyl acetate. All the literature values for the density appear to be too large relative to the measurements made in this research.

A critical temperature of (600 ± 1.0) K (Table 5 and Figure 2) was obtained from the dsc measurements. A corresponding critical pressure of 2685 kPa (Table 5) was derived using the fitting procedures outlined above. Quadri and Kudchadker (1991) observed corresponding values of (599.9 ± 0.4) K and (2770 ± 20) kPa using a "modified Kay-type apparatus". The agreement on the critical temperature is excellent. Agreement on the critical pressure of pentyl acetate is not as good but probably relates to its decomposition on prolonged resident time in the region of the critical point.

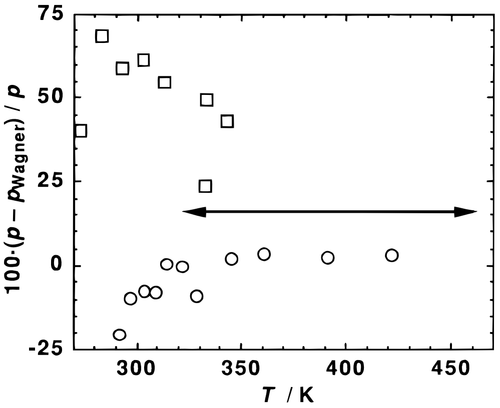

Figure 6. Comparison of literature vapor pressures for pentyl acetate with those obtained using the Wagner equation and the parameters listed in Table 5. The double-headed arrow represents the range of the measurements reported in Table 1. Key: (△) Schmidt, G. *Z. Phys. Chem. Stoechiom. Verwandtschaftsl.* **1926**, *121*, 221−253; (○) Brozena, A.; Walker, H. M.; Penski, E. C. *Vapor pressures of n-amyl acetate: Literature review and Experimental Determination*. CRDEC-TR-320, 1992; 43 pp. Available from NTIS Order No. AD-A247232. Both references and the corresponding sets of measured values were obtained in a communication from the Editor.

Note on a Method To Estimate the Temperature of the Onset of Thermal Decomposition via Radical Formation. From numerous ebulliometric vapor-pressure measurement studies at Bartlesville, both published (Chirico et al., 1989b) and unpublished, it has been shown that for alkanes with chain length >10, thermal decomposition is initiated at 625 K. (In this context the thermal decomposition point is defined as the temperature at which the difference between the boiling and condensation temperatures in the ebulliometric apparatus starts to deviate rapidly with time. Usually, the difference rises from a few milli-Kelvin to several tenths of a Kelvin in the space of 10 min.)

For a unimolecular scission reaction of a molecule into two radicals, the rate of reaction (Benson and O'Neal, 1970) can be expressed as

$$\ln(k/{\rm s}^{-1}) = 33.2 - ({\rm BDE}/RT) \qquad (5)$$

where BDE = the bond dissociation energy in J·mol^{-1} and R is the gas constant in units of J·K^{-1}·mol^{-1}. For long chain alkanes the C−C bond dissociation energy is approximately 336 kJ·mol^{-1} [(80.4 ± 2) kcal·mol^{-1} see McMillan and Golden (1982)]. Hence, at 625 K

$$\ln(k/{\rm s}^{-1}) = 33.2 - (336000/625R)$$

or $k = 2 \times 10^{-14}\ {\rm s}^{-1}$ or $t_{1/2}$, one half life, of >1 million years! However, it must be remembered that each bond scission leads to a chain reaction in which each of the two radicals formed abstracts atoms from other molecules of the compound, giving additional radicals. This can continue until radicals combine in pairs in the "termination step".

A complete kinetic analysis of the system is beyond the scope of the research described in this report but the observation of a constant decomposition temperature for normal alkanes greater than C_{10} can be used to derive a "rule-of-thumb" to estimate either bond dissociation energies or thermal decomposition onset temperatures. In an approximate form, eq 5 can be written as

$$\ln(2 \times 10^{-14}) = -31.5 = 33.2 - (\mathrm{BDE}/RT)$$

or

$$\mathrm{BDE} = 64.7RT$$

or

$$T = \mathrm{BDE}/(64.7R)$$

Using the "rule-of-thumb" for the results obtained for ethyl octyl sulfide where (see above) a thermal decomposition temperature of approximately 552 K was noted, a C−S bond dissociation energy of 297 kJ·mol^{-1} is calculated. In reverse using the C−S bond dissociation energy of (308 ± 9) kJ·mol^{-1} listed (Griller et al., 1990) for Et−SR compounds a thermal decomposition temperature of (576 ± 17) K is estimated. Agreement between the "rule-of-thumb" and experimental observation is excellent.

The above "rule-of-thumb" applies *only* in cases where thermal decomposition is initiated by bond scission and radical formation. In cases where decomposition occurs by another mechanism such as condensation the "rule-of-thumb" obviously will not apply.

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