Vapor Pressures, Liquid Densities, Liquid Heat Capacities, and Ideal Gas Thermodynamic Properties for 3-Methylhexanal and 3,4-Dimethylpentanal

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Vapor pressures, liquid densities, and liquid heat capacities were measured for 3-methylhexanal and 3,4-dimethylpentanal which are two of several C_7 aldehyde reaction products that can be obtained from the hydroformylation of hexenes using cobalt or rhodium homogeneous catalyst precursors. The vapor pressure data were fitted to the Miller and Antoine equations and also compared to predictions obtained from the Riedel–Plank–Miller equation. Values for the critical temperature and critical pressure were derived by group contribution methods and compared to independent values obtained by fitting the vapor pressure data to the Riedel–Plank–Miller equation and two corresponding-states-based equations. The liquid density data were compared to predictions obtained from the Yen–Woods equation and were also fitted to an empirical equation. Predictions from the Sterling-Brown, Yuan and Stiel, and the Rowlinson corresponding-state correlations were in good agreement with the liquid heat capacity data, although an empirical polynomial equation was also tested and had a lower mean deviation. Ideal gas thermodynamic properties were also derived and were used to calculate some of the predicted quantities.

Introduction

Hydroformylation of olefins with cobalt or rhodium homogeneous catalysts is an efficient method for producing aldehydes with applications ranging from laboratory-scale synthesis to industrial processing (*1*). A knowledge of the pure-component physical properties of the reactant olefins and product aldehydes is essential in any application involving this class of reactions such as evaluation of reaction kinetics, reactor engineering, and design of separation systems. Although some of the pure-component physical properties for the C_2–C_7 olefins and C_2–C_5 aldehydes are available (*2*), fundamental data for the various aldehyde isomers within the C_6–C_8 range are either lacking or have not been reported in the open literature. Several new processes that involve hydroformylation of branched hexenes have recently been proposed (*3*), thereby providing the incentive to procure and correlate physical properties for the resulting branched C_7 aldehydes.

The objective of this study is to provide vapor pressure, liquid density, and liquid heat capacity data for 3-methylhexanal and 3,4-dimethylpentanal which are two of the 33 possible C_7 aldehyde isomers. Another objective is to determine correlation equation constants by using the experimental data as the basis and to compare the results to those obtained from generalized correlations. A final objective is to derive critical constants and ideal-gas thermodynamic properties such as heat capacity, enthalpy of formation, entropy of formation, and Gibbs free energy of formation by using available group contribution methods and to correlate the results where appropriate.

Experimental Section

Materials. Preparation of 3-methylhexanal and 3,4-dimethylpentanal was performed in a 0.3-L 316 stainless steel autoclave by hydroformylation of 2-methyl-1-pentene and 2,3-dimethyl-1-butene in separate experiments. For this and other related hydroformylations, the olefin reactant was used as received from commercial sources without further treatment. In a typical run, 0.75 g of $HRhCO[(C_6H_5)_3P]_3$ catalyst precursor, 36 g of $(C_6H_5)_3P$ promoter, and 100 g of the olefin reactant were charged to the autoclave in the presence of a nitrogen purge. The reactor was sealed, pressurized to 2757 kPa (400 psig) by using a 1:1 H_2/CO gas mixture, and heated to 393.15 K (120 °C). The pressure was then increased to 3447 kPa (500 psig) and the reaction was allowed to proceed until no further gas uptake from the supply reservoir was detected (about 4 h). The reactor was then cooled and the bottled product was placed in a dry ice–acetone bath to precipitate the catalyst and excess promoter from solution. The liquid was recovered by filtration and distilled by slowly decreasing the pressure from atmospheric to 10–20 mmHg vacuum and collecting distillate fractions. GC analysis of the fractions was performed with a Varian 3700 using a special dual-column switching method which is described in detail elsewhere (*4*). Positive identification of the aldehyde was performed by using GCMS. The purity of the individual aldehydes used in subsequent physical property determinations was in excess of 99 mol %.

Thermal Stability Measurements. Each of the aldehydes was examined to define the temperature limits where thermal decomposition would occur. This was performed by using a specially designed instrument that is based upon accelerating rate calorimetry. The primary function of the instrument is to maintain a sample of the material being tested in an adiabatic state and to permit the sample to undergo thermal reaction or decomposition while recording the pressure and temperature of the sample container as a function of time. In a typical experiment, the sample of the pure aldehyde was placed in a spherical bomb constructed of Pyrex glass in the presence of an inert gas. After connection to appropriate temperature and pressure sensing devices, the sample temperature was increased to a preset search temperature at which time a three-step sequence consisting of a 10-min wait, 20-min search, and 5 °C temperature increase was initiated. This sequence was repeated until a self-heating rate of 0.01 °C/min or greater was sensed. The sample was then maintained at an adiabatic state until the self-heating rate dropped below 0.008 °C/min. The three-step sequence and the adiabatic modes were alternately used until either the bomb pressure increased or the sample temperature exceeded predetermined values. For the two aldehydes of interest here, no gas evolution was detected until T = 498.15 K (225 °C) which defines the upper limit for thermal stability of these materials. Sample bombs constructed of Hastelloy C yielded gas evolution at T = 398.15 K (125 °C) for a related aldehyde (n-heptanal) so subsequent experiments were performed using glass for all wetted parts.

Vapor Pressure Measurements. The vapor pressure measurements were performed using a Hoover-John-Mellen semimicro ebulliometer with about 0.003 L of sample. Data were collected at a series of discrete temperatures over a range of

0021-9568/87/1732-0266$01.50/0

Table I. Vapor Pressure of Hexadecane

	P, kPa		
T, K	exptl	lit.[a]	ϵ[b]
388.95	0.252	0.252	0.00
411.55	0.805	0.803	−0.34
430.45	1.916	1.913	−0.14
447.95	3.892	3.918	0.68
462.25	6.652	6.686	0.52
476.35	10.738	10.831	0.86
502.55	24.013	24.218	0.85
520.55	39.693	39.651	−0.10
540.95	65.317	65.832	0.78
541.35	66.635	66.504	−0.20
560.25	101.861	101.842	−0.02
			max dev[b] 0.86
			mean dev[c] 0.41

[a] From Tables 23-2(1.101)-Ka, 23-2(1.01)-K in ref *2*. [b] ϵ = pressure deviation = $100(P_{\text{lit.}} - P_{\text{exptl}})/P_{\text{lit.}}$. [c] $100\sum_i(|P_{\text{lit.}} - P_{\text{exptl}}|/P_{\text{lit.}})_i/n$.

Table II. Liquid Heat Capacity of Diphenyl Ether

	C_{pL}, cal mol^{-1} K^{-1}		
T, K	exptl	lit.[a]	ϵ[b]
323.15	66.037	66.547	0.766
343.15	67.891	68.707	1.188
363.15	70.102	70.885	1.105
383.15	71.837	73.045	1.654
403.15	74.389	75.172	1.042
423.15	77.111	77.349	0.308
			max dev[b] 1.654
			mean dev[c] 1.011

[a] From ref *25*. [b] ϵ = heat capacity deviation = $100(C_{pL,\text{lit.}} - C_{pL,\text{exptl}})/C_{pL,\text{lit.}}$. [c] $100\sum_i(|C_{pL,\text{lit.}} - C_{pL,\text{exptl}}|/C_{pL,\text{lit.}})_i/n$.

0.667 kPa (5 mmHg), or an initial pressure which corresponded to a boiling point of 323.15 K, to 101.32 kPa (760 mmHg). The pressure was measured with a Texas Instruments fused quartz pressure gauge which had a worst case precision of ±0.0053 kPa (±0.04 mmHg). A glass-sheathed platinum RTD probe having an accuracy of ±0.02 K was used for temperature sensing. An Omega temperature indicator having an accuracy of ±0.01 K was used to display the temperature. The temperature variation during a series of measurements typically ranged from 0.01 to 0.2 K. The accuracy of the measurements was checked by using hexadecane as a reference material. A comparison between experimental and literature results is given in Table I where it can be seen that the maximum deviation is 0.86% with a mean deviation of 0.41%. The vapor pressure data for the C_7 aldehydes can be expected to have similar errors based upon the hexadecane results.

Density Measurements**.** Density measurements for each aldehyde were made over the range 298.15–423.15 K using calibrated stem pycnometers immersed in a thermostated bath whose temperature was maintained within ±0.1 K. A D & A bridge platinum RTD was used for sensing the bath temperature and an Omega temperature indicator having an accuracy of ±0.1 K was used to display the temperature. The estimated error in the density values for the C_7 aldehydes is ±0.002 g cm^{-3}.

Liquid Heat Capacity Measurements**.** The liquid heat capacity of each aldehyde was measured over the range 303.15–423.15 K by differential scanning calorimetry using a Perkin-Elmer DSC-2C. The sample was encapsulated in a gold pan under ambient conditions prior to the experiment. The heat capacity was calculated by comparison to a sapphire specific heat capacity standard. The accuracy of the instrument was tested by using diphenyl ether as a reference material and performing measurements over the same temperature range indicated above. The results are given in Table II and have a maximum deviation of 1.654% and a mean deviation of 1.010% when compared to the indicated literature values. The heat capacity data for the individual C_7 aldehydes can be expected to have similar errors based upon the diphenyl ether results.

Table III. Normal Boiling Temperatures and Critical Constants for C_7 Aldehydes

	T_b, K					P_c,[e]	
compd	obsd[a]	est[b]	ϵ[c]	T_c,[d] K	T_c,[e] K	atm	V_c[e]
3-methylhexanal	417.46	424.64	−1.72	605.42	595.18	28.292	439
3,4-dimethylpentanal	417.25	423.44	−1.48	608.48	599.59	28.777	435

[a] From vapor pressure data. [b] From eq 1. [c] ϵ is the boiling point deviation = $100(T_{b,\text{obsd}} - T_{b,\text{est}})/T_{b,\text{obsd}}$. [d] Fedors method (*7*). [e] Lydersen's method (*5*).

Results and Discussion

Normal Boiling Temperatures and Critical Properties**.** Table III lists values for the normal boiling temperatures and critical constants for each compound. The normal boiling temperatures were first determined by fitting the vapor pressure data to the Antoine equation (described below) and determining the saturation temperature at P = 101.32 kPa (1 atm). For comparison purposes, the normal boiling temperature was also calculated by using eq 1. For this case, the reduced boiling point T_{br} was

$$T_b = T_{br}T_c \qquad (1)$$

obtained by using the group contribution method of Lydersen (*5*) as described by Reid et al. (*6*), while the critical temperature T_c was obtained by using Fedors' method (*7*). The results show that 3-methylhexanal has a slightly greater boiling point than 3,4-dimethylpentanal. Boiling point data for lower carbon number aldehydes (*2*) show that, for a given carbon number, the normal boiling temperature is greatest for the linear isomer and decreases with increasing branching along the carbon skeletal chain. On the basis of this observation, one would expect 3-methylhexanal to have a greater normal boiling temperature than 3,4-dimethylpentanal which agrees with both the experimental and estimated values for T_b. The estimated values for T_b are greater than those derived from vapor pressure data, but the absolute deviations are less than 1.8%. Values for the critical compressibility Z_c were obtained from the estimated values of P_c, V_c, and T_c by using eq 2.

$$Z_c = \frac{P_cV_c}{RT_c} \qquad (2)$$

Experimental determination of the critical properties for aldehydes is either impossible or extremely difficult since these substances can readily decompose to lower boiling fragments or undergo condensation to higher boiling products. As a result, the available group contribution methods for estimation of critical properties contain a group contribution value for the aldehyde moiety which has little or no experimental basis. In fact, critical temperatures for aldehydes have only been measured for acetaldehyde (*8*) and benzaldehyde (*9*), and these are unreliable because of the rapid decomposition of these species at elevated temperature and pressure. For these reasons, the values for the critical properties derived in this work which are given in Table III may contain errors larger than the general range of errors given in Table 2-2 of Reid et al. (*6*) which are claimed to apply for Lydersen's method. The derived values for critical properties are used in this work, however, since the other available group contribution methods are subject to errors of these magnitudes when applied to aldehydes and, at present, the experimental determination of the critical properties by available methods is improbable.

Table IV. Vapor Pressure of 3-Methylhexanal

obsd		ϵ,[a] %		
T, K	P, kPa	Miller eq	Antoine eq	RPM[c] eq
314.50	1.987	-0.37	-0.63	16.36
318.10	2.433	0.93	0.85	16.55
323.20	3.102	-0.74	-0.63	13.85
328.60	4.065	-0.11	0.12	13.04
339.30	6.664	0.05	0.37	10.62
348.70	9.990	0.32	0.57	8.73
361.90	17.339	3.13	3.16	8.68
363.35	17.356	-2.21	-2.21	3.36
374.90	26.013	-2.29	-2.50	1.27
386.40	40.037	0.72	0.38	2.63
402.60	66.585	0.88	0.63	1.41
417.35	101.014	-0.02	0.24	0.13
417.65	101.606	-0.41	-0.13	-0.25

	Miller eq	Antoine eq	RPM eq
max dev[a]	3.13	3.16	16.55
mean dev[b]	0.94	0.95	7.45

[a] ϵ = pressure deviation = $100(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}$. [b] $100\sum_i(|P_{\text{exptl}} - P_{\text{calcd}}|/P_{\text{exptl}})_i/n$. [c] Riedel–Plank–Miller equation.

Table V. Vapor Pressure of 3,4-Dimethylpentanal

obsd		ϵ,[a] %		
T, K	P, kPa	Miller eq	Antoine eq	RPM eq
319.07	2.681	0.00	0.14	13.63
333.28	5.354	0.41	0.31	11.23
342.40	8.027	0.35	0.23	9.58
342.79	8.038	-1.20	-1.32	8.11
354.75	13.355	0.30	0.26	7.59
365.40	20.021	0.18	0.22	5.95
373.40	26.651	0.13	0.22	4.84
385.58	40.061	0.03	0.16	3.25
402.35	66.823	-0.11	-0.06	1.24
402.39	66.805	-0.25	-0.20	1.10
417.38	101.650	0.17	-0.02	-0.04

	Miller eq	Antoine eq	RPM eq
max dev[a]	-1.20	-1.32	13.63
mean dev[b]	0.28	0.29	6.05

[a] ϵ = pressure deviation = $100(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}$. [b] $100\sum_i(|P_{\text{exptl}} - P_{\text{calcd}}|/P_{\text{exptl}})_i/n$.

Vapor Pressures. The vapor pressure data for each aldehyde are presented in Tables IV and V. Included also are the relative errors obtained when the Miller (*10*), Antoine (*11*), and the Riedel–Plank–Miller (RPM) (*12*) vapor pressure equations were used to interpret the results. The following forms of these equations were used:

Miller equation

$$\ln P = A_m + B_m/T + C_mT + D_mT^2 \tag{3}$$

Antoine equation

$$\ln P = A_a + B_a/(T + C_a) \tag{4}$$

Riedel–Plank–Miller equation

$$\ln \frac{P}{P_c} = -\frac{G}{T_r}[1 - T_r^2 + k(3 + T_r)(1 - T_r)^3] \tag{5}$$

The constants in the Miller equation were determined by linear least squares using the ln P vs. T data, while the Antoine equation constants were determined by nonlinear regression. Initial estimates for the Antoine constant A_a, B_a, and C_a were determined by linear regression using the following linearized form of eq 4

$$T \ln P = A_aT + D_a - C_a \ln P \tag{6}$$

where

$$D_a = A_aC_a + B_a \tag{7}$$

The RPM equation constants G and k were determined from the following formulas (*6*, *12*) which require values for the normal boiling temperature T_b and the critical constants P_c and T_c

$$h = T_{br}\frac{\ln P_c}{1 - T_{br}} \tag{8}$$

$$G = 0.4835 + 0.4605h \tag{9}$$

$$k = \frac{h/G - (1 + T_{br})}{(3 + T_{br})(1 - T_{br})^2} \tag{10}$$

Values of the constants for all three equations are given in Table VI along with the percent root mean square deviation.

The results in Tables IV–VI show that the mean deviation and root mean square deviation for each aldehyde increase in the order of Miller, Antoine, and Riedel–Plank–Miller equation. The errors obtained when the Miller equation is used are only slightly less than those for the Antoine equation since the former one has an additional adjustable parameter. The RPM equation has errors which are an order of magnitude greater and which show a systematic decreasing error as the normal boiling temperature is approached. One possible reason for the discrepancy may be attributed to errors in the estimated critical properties. This aspect is considered in more detail below.

Alternate Determination of the Critical Properties. As mentioned previously, there is a lack of precise critical property data for aldehydes so that derived values based upon group contribution methods may be unreliable. The larger errors associated with the RPM equation, whose constants were derived from the experimentally measured normal boiling temperature and critical properties derived from Lydersen's method, seem to suggest that the critical properties used as input parameters may be the primary reason for these errors. A brief investigation was conducted to determine whether the errors could be reduced by deriving alternate values for the critical properties which were not based upon group contribution methods. The techniques used here were based upon extrapolation of the experimental vapor pressure data to the critical point using data

Table VI. Miller, Antoine, and Riedel–Plank–Miller Vapor Pressure Equation Constants

compd	Miller const	Antoine const	RPM const
3-methylhexanal	$A_m = 0.418097 \times 10^2$ $B_m = -0.829544 \times 10^4$ $C_m = -0.633482 \times 10^{-1}$ $D_m = 0.523705 \times 10^{-4}$	$A_a = 0.147153 \times 10^2$ $B_a = -0.371490 \times 10^4$ $C_a = -0.495800 \times 10^2$	$h = 0.785164 \times 10^1$ $G = 0.409918 \times 10^1$ $k = 0.648491$
prms[a]	3.38	3.44	26.87
3,4-dimethylpentanal	$A_m = 0.261046 \times 10^2$ $B_m = -0.644726 \times 10^4$ $C_m = -0.184080 \times 10^{-1}$ $D_m = 0.944519 \times 10^{-5}$	$A_a = 0.140503 \times 10^2$ $B_a = -0.333000 \times 10^4$ $C_a = -0.642000 \times 10^2$	$h = 0.768774 \times 10^1$ $G = 0.402371 \times 10^1$ $k = 0.628202$
prms[a]	0.94	0.95	20.07

[a] Percent root mean square deviation defined by $100[\sum_i((P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}})_i^2/n]^{1/2}$.

measured over a limited temperature range where the aldehydes are known to be stable. Some particular methods for extrapolation of vapor pressures for estimation of critical temperature and pressure include unconstrained fitting and extrapolation (*13*), constrained extrapolation (*14*), and corresponding-states schemes using one or two reference fluids (*15*, *16*). A two-fluid corresponding-states scheme using reference fluids whose chemical type and acentric factor match the fluid under study has been shown (*15*) to produce critical pressures whose errors are about the same as those produced by the method of constrained extrapolation (*14*). In addition, the working equations for the two-fluid corresponding-states scheme are easier to implement when compared to those for the method of constrained extrapolation. For these reasons, the two-fluid corresponding-states scheme was selected over the method of constrained extrapolation in this work.

According to the two-fluid reference scheme, the vapor pressure is evaluated from the following equation where the reference substances are denoted by subscripts 1 and 2

$$\ln P = \ln P_c + (\ln P_{r,2} - \ln P_{r,1})(\omega - \omega_1)/(\omega_2 - \omega_1) \qquad (11)$$

Values for the critical pressure P_c and acentric factor ω are calculated by minimization of an objective function defined in terms of the square of the relative errors between the predicted values from eq 11 and the logarithm of the experimental vapor pressure data using standard linear least-squares procedures. Once the critical pressure and acentric factor are determined, the critical temperature is calculated from the defining relation for the acentric factor

$$\omega = -\frac{\ln (P_r(T_r = 0.7)}{\ln 10} - 1 \qquad (12)$$

If the Antoine equation gives a satisfactory representation of the experimental vapor pressure in proximity of $T_r = 0.7$, then the following explicit expression for the critical temperature can be developed from eq 12 where A_a, B_a, and C_a are the Antoine equation constants

$$T_c = \frac{1}{0.7}\left[\frac{B_a}{\ln P_c - A_a - (1 + \omega) \ln 10} - C_a\right] \qquad (13)$$

For comparison purposes, values for the critical temperature and pressure were also determined from the corresponding-states vapor pressure equation of Lee and Kesler (*16*)

$$\ln P = \ln P_c + f^{(0)}(T_r) + \omega f^{(1)}(T_r) \qquad (14)$$

The functions $f^{(0)}(T_r)$ and $f^{(1)}(T_r)$ are expressed as empirical polynomials in the reduced temperature and are omitted here for brevity. The acentric factor which appears in eq 14 is expressed as a ratio of two empirical functions by eq 2-3.4 in Reid et al. (*6*) where the critical pressure P_c and reduced boiling temperature T_{br} appear as parameters. If the critical pressure and critical temperature are viewed as adjustable constants, the same objective function described above can be minimized by the use of nonlinear least squares such as Marquardt's method (*17*) using the experimental vapor pressure data given in Tables IV and V as the basis. This method will yield a second independent set of values for P_c, T_c, and ω for comparison purposes.

Table VII. Determination of Critical Properties and Acentric Factor for 3-Methylhexanal by Three Methods

obsd		ϵ,[a] %		
T, K	P, kPa	two-fluid corresp-states, eq	Lee–Kesler eq	RPM eq
314.50	1.987	0.00	−0.80	−0.81
318.10	2.433	1.26	0.77	0.77
323.20	3.102	−0.47	−0.60	−0.60
328.60	4.065	0.03	0.20	0.20
339.30	6.664	−0.02	0.48	0.48
348.70	9.990	0.03	0.64	0.64
361.90	17.339	2.61	3.14	3.14
363.35	17.356	−2.79	−2.24	−2.24
374.90	26.349	−2.98	−2.63	−2.62
386.40	40.037	0.12	0.20	0.21
402.60	66.585	0.77	0.44	0.45
417.35	101.148	0.82	0.13	0.13
417.65	101.606	0.46	−0.24	−0.24

	Lydersen's method	two-fluid eq	Lee–Kesler eq	RPM eq
max dev[a]		−2.98	3.14	3.14
mean dev[b]		0.95	0.96	0.96
P_c, atm	28.292	56.52	58.58	68.99
T_c, K	595.18	661.98	668.01	678.37
ω		0.266	0.246	0.251

[a] ϵ = pressure deviation = $100(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}$. [b] $100\sum_i(|P_{\text{exptl}} - P_{\text{calcd}}|/P_{\text{exptl}})_i/n$.

Table VIII. Determination of Critical Properties and Acentric Factor for 3,4-Dimethylpentanal by Three Methods

obsd		ϵ,[a] %		
T, K	P, kPa	two-fluid corresp-states eq	Lee–Kesler eq	RPM eq
319.07	2.681	−0.20	−0.20	−0.16
333.28	5.354	0.30	0.45	0.44
342.40	8.027	0.37	0.48	0.47
342.79	8.038	−1.18	−1.06	−1.07
354.75	13.355	0.52	0.52	0.52
365.40	20.021	0.53	0.43	0.43
373.40	26.651	0.55	0.38	0.38
373.93	26.712	−1.07	−1.25	−1.24
385.58	40.061	0.47	0.23	0.25
402.35	66.823	0.16	−0.07	−0.05
402.39	66.805	0.02	−0.21	−0.19
417.38	101.650	0.09	−0.03	−0.03
417.56	101.434	−0.61	−0.72	−0.72

	Lydersen's method	two-fluid eq	Lee–Kesler eq	RPM eq
max dev[a]		−1.18	−1.25	−1.24
mean dev[b]		0.47	0.46	0.46
P_c, atm	28.777	52.82	28.55	35.02
T_c, K	599.59	660.32	609.07	623.13
ω		0.260	0.353	0.336

[a] ϵ = pressure deviation = $100(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}$. [b] $100\sum_i(|P_{\text{exptl}} - P_{\text{calcd}}|/P_{\text{exptl}})_i/n$.

The third and final method that was investigated involved the application of nonlinear least squares to the RPM equation where the critical pressure and critical temperature were used as adjustable parameters. The boiling temperatures listed in Table III that were derived from the experimental data by using the Antoine equation were employed in the expressions for h and k in eq 8 and 10, respectively. Estimates for T_c and P_c needed to initiate the parameter search for Marquardt's method (*17*) were assumed to be the Lydersen-based values given in Table III. This represents an application of unconstrained extrapolation analogous to that used by Ambrose (*13*).

Tables VII and VIII compare the errors obtained when the above three methods are applied to the vapor pressure data for the two aldehydes. Included also are the values for the critical pressure, critical temperature, and the acentric factor obtained for each method from the least-squares procedures by fitting the vapor pressure data over the limited experimental range. In the case of the two-fluid method, benzaldehyde and carbon disulfide were chosen as the reference fluids since their critical properties and acentric factors were both above and below the fitted values for the aldehydes. Trial calculations using compounds that were related to the aldehydes such as 3-methylhexane, *n*-heptane, 1-heptanol, and a few others resulted in larger errors between the experimental and predicted vapor pressures. Since the two-fluid equation given by eq 11 has the form of a linear interpolation function, one would expect the best results to be obtained when the reference lines are above and below those for the unknown fluid. Although this may sometimes be achieved with reference fluids having a chemical structure that is similar to the fluid whose critical properties and acentric factor are to be determined, our experience suggested this criteria sometimes produced poor quality fits.

Inspection of the results given in Tables VII and VIII shows that all three methods give mean deviations that are within 0.01% of each other for a given aldehyde. The absolute values of the errors on a point-by-point basis are also in good agreement with those given in Tables IV and V for the Antoine and Miller vapor pressure equations for each aldehyde.

Comparisons of the critical properties and acentric factors obtained for a given aldehyde produced some mixed results. By using the critical temperature and critical pressure as adjustable constants in the RPM equation, the errors between the experimental and predicted values for the vapor pressures were significantly reduced. This can be seen by comparing the last column in Tables IV and V with the last column in Tables VII and VIII. In the case of 3-methylhexanal, the Lydersen values for critical pressure and critical temperature had to be increased by factors of 68.99/28.292 = 2.44 and 678.37/595.18 = 1.14, respectively, until good agreement between the experimental and predicted vapor pressure data was obtained. Results for the other methods produces ratios for P_c and T_c that, when compared to Lydersen-based values, have similar magnitudes. The value of the acentric factor produced by the RPM equation is 0.251 which seems quite reasonable. In addition, this value lies between the acentric factors obtained by the two reference fluid corresponding-states method and the Lee–Kesler vapor pressure equation. Those values for P_c, T_c, and ω obtained from the two-fluid and Lee–Kesler equations are in better agreement when compared to each other, but both are based upon similar principles and this degree of self-consistency might be expected. That the critical pressure for all three methods differs so greatly from the Lydersen value suggests that further work is needed to resolve these differences.

Comparison of the critical properties and acentric factors derived from the data for 3,4-dimethylpentanal given in Table VIII show some slightly different trends than those for 3-methylhexanal. The critical pressure values obtained by fitting the Lee–Kesler equation and the Riedel–Plank–Miller equation are in reasonable agreement with the Lydersen-derived value, while the two-fluid-based value for P_c differs by a factor of 52.82/28.28 = 1.84. Similar trends are observed for the critical temperature with T_c values from the Lee–Kesler equation and RPM equation being between 6 and 10 K greater than the Lydersen-derived value. By contrast, the T_c value from the two-fluid equation is about 60 K greater.

Since the Lee–Kesler and RPM equations have a different theoretical basis, the agreement between the two methods in terms of the critical properties and acentric factors appears quite reasonable. This is reinforced by the derived values for P_c and T_c obtained by Lydersen's method which yield errors within the ranges suggested in Table 2-2 of Reid et al. (*6*) when compared to the fitted values obtained from the Lee–Kesler equation and RPM equation.

Table IX. Liquid Densities of 3-Methylhexanal

obsd		ϵ,[d] %		
T, K	ρ, g cm^{-3}	Yen–Woods[a]	Yen–Woods[b]	empirical[c]
298.15	0.813	3.37	0.00	−0.01
303.20	0.808	3.26	−0.11	−0.07
313.20	0.800	3.28	−0.09	0.04
323.20	0.791	3.20	−0.18	0.03
348.10	0.769	3.12	−0.26	0.05
373.10	0.746	3.06	−0.32	−0.05

	Yen–Woods[a]	Yen–Woods[b]	empirical[c]
max dev[d]	3.37	−0.32	−0.07
mean dev[e]	3.86	0.19	0.05

[a] From eq 15. [b] From eq 18 with T_{ref} = 298.15 K. [c] From eq 16. [d] ϵ = density deviation = $100(\rho_{exptl} - \rho_{calcd})/\rho_{exptl}$. [e] $100\sum_i(|\rho_{exptl} - \rho_{calcd}|/\rho_{exptl})_i/n$.

Table X. Liquid Densities of 3,4-Dimethylpentanal

obsd		ϵ,[d] %		
T, K	ρ, g cm^{-3}	Yen–Woods[a]	Yen–Woods[b]	empirical[c]
298.15	0.824	3.60	0.00	−0.04
303.15	0.820	3.61	0.01	0.01
313.20	0.811	3.52	−0.09	0.00
323.20	0.802	3.43	−0.17	−0.02
348.20	0.781	3.49	−0.12	0.14
373.30	0.757	3.31	−0.30	−0.09

	Yen–Woods[a]	Yen–Woods[b]	empirical[c]
max dev[d]	3.61	−0.30	0.14
mean dev[e]	3.49	0.12	0.05

[a] From eq 15. [b] From eq 18 with T_{ref} = 298.15 K. [c] From eq 16. [d] ϵ = density deviation = $100(\rho_{exptl} - \rho_{calcd})/\rho_{exptl}$. [e] $100\sum_i(|\rho_{exptl} - \rho_{calcd}|/\rho_{exptl})_i/n$.

Additional vapor pressure data of high precision over a more broad range of temperatures where decomposition of the aldehydes is absent are needed before a more detailed comparison of critical property values can be made. However, until these data and suitable interpretation become available, the evidence given here in one case suggests that the group contribution values provide a first estimate that should be viewed with some caution when applied to this class of compounds.

Liquid Density Data. Tables IX and X contain the experimental liquid density data for each compound along with the relative errors obtained when the Yen–Woods (*18*) and an empirical equation form were used to interpret the results. The particular equation forms used here are given below.

Yen–Woods equation

$$\rho_s = \rho_c[1 + \sum_{j=0}^{4} K_j(1 - T_r)^{j/3}] \tag{15}$$

Empirical equation

$$\rho_s = A + BT \tag{16}$$

If a density value is available at a given reference temperature, then the critical density ρ_c can be obtained from eq 15

$$\rho_c = \rho_{s,ref}[1 + \sum_{j=0}^{4} K_j(1 - T_{r,ref})^{j/3}]^{-1} \tag{17}$$

Substitution of eq 17 into eq 15 gives the following modified Yen–Woods form which does not have an explicit dependence on ρ_c.

$$\rho_s = \rho_{s,ref}\frac{1 + \sum_{j=0}^{4} K_j(1 - T_r)^{j/3}}{1 + \sum_{j=0}^{4} K_j(1 - T_{r,ref})^{j/3}} \tag{18}$$

The constants K_j in eq 15, 17, and 18 are polynomial functions of the critical compressibility Z_c and are given elsewhere (*6*,

Table XI. Yen–Woods and Empirical Liquid Density Equation Constants

compd	Yen–Woods[a]	Yen–Woods[b]	empirical[c]
3-methylhexanal	$a_0 = 0.260112$	$a_0 = 0.269187$	$A = 0.107828 \times 10^{1}$
	$a_1 = 0.479179$	$a_1 = 0.495898$	$B = -0.889602 \times 10^{-3}$
	$a_2 = 0.212730$	$a_2 = 0.220153$	
	$a_3 = 0.0$	$a_3 = 0.0$	
	$a_4 = 0.291739 \times 10^{-1}$	$a_4 = 0.301918 \times 10^{-1}$	
prms[d]	0.0322	0.002	4.68×10^{-4}
3,4-dimethylpentanal	$a_0 = 0.262503$	$a_0 = 0.272309$	$A = 0.108891 \times 10^{1}$
	$a_1 = 0.483382$	$a_1 = 0.501439$	$B = -0.887335 \times 10^{-3}$
	$a_2 = 0.214493$	$a_2 = 0.222505$	
	$a_3 = 0.0$	$a_3 = 0.0$	
	$a_4 = 0.296352 \times 10^{-1}$	$a_4 = 0.307423 \times 10^{-1}$	
prms[d]	0.035	0.002	7.19×10^{-4}

[a] From eq 15 with ρ_c estimated from Lydersen's method. [b] From eq 15 with ρ_c obtained from eq 17. [c] From eq 16. [d] Percent root mean square deviation defined by $100[\sum_i((\rho_{\mathrm{exptl}} - \rho_{\mathrm{calcd}})/\rho_{\mathrm{exptl}})_i^2/n]^{1/2}$.

Table XII. Ideal Gas Enthalpy of Formation, Entropy, Entropy of Formation, Gibbs Free Energy of Formation, and Heat Capacity for C_7 Aldehydes

					$C_p°$, cal mol^{-1} K^{-1}					
compd	$\Delta H_f°$, kcal mol^{-1}	$S°$, cal mol^{-1} K^{-1}	$\Delta S_f°$,[a] kcal mol^{-1}	$\Delta G_f°$,[b] kcal mol^{-1}	300 K	400 K	500 K	600 K	800 K	1000 K
3-methylhexanal	−64.66	109.13	252.51	−21.91	41.15	51.15	59.99	67.51	79.75	88.67
3,4-dimethylpentanal	−65.94	106.45	252.51	−22.39	40.88	51.09	60.06	67.65	79.94	88.81

[a] $\Delta S_f° = S° - \sum_i \nu_i S°_{e,i}$. [b] $\Delta G_f° = \Delta H_f° - T\Delta S_f°$, eq 20.

Table XIII. Constants in the Ideal Gas Heat Capacity Polynomial

compd	heat capacity polynomial constants[a]
3-methylhexanal	$a_0 = 0.916477$
	$a_1 = 0.158590$
	$a_2 = -0.923968 \times 10^{-4}$
	$a_3 = 0.215288 \times 10^{-7}$
	$a_4 = 0.350277 \times 10^{5}$
prms[b]	4.445×10^{-4}
3,4-dimethylpentanal	$a_0 = 0.231085$
	$a_1 = 0.161375$
	$a_2 = -0.949815 \times 10^{-4}$
	$a_3 = 0.221734 \times 10^{-7}$
	$a_4 = 0.166052 \times 10^{k}$
prms[b]	4.727×10^{-4}

[a] Equation 21. [b] Percent root mean square deviation defined by $100[\sum_i((C_p°_{\mathrm{est}} - C_p°_{\mathrm{calcd}})/C_p°_{\mathrm{est}})_i^2/n]^{1/2}$.

Table XIV. Liquid Heat Capacities of 3-Methylhexanal

obsd		ϵ[e]			
T, K	$C_{p\mathrm{L}}$, cal mol^{-1} K^{-1}	Bondi eq[a]	Sternling–Brown eq[b]	Yuan–Stiel eq[c]	empirical[d]
323.15	58.78	−1.06	−2.67	−3.97	0.55
328.15	58.93	−1.56	−3.24	−4.25	0.09
333.15	59.50	−1.34	−3.07	−3.78	0.31
338.15	59.80	−1.59	−3.39	−3.84	0.02
343.15	59.95	−2.08	−3.98	−4.16	−0.56
348.15	60.82	−1.37	−3.33	−3.25	0.02
353.15	60.95	−1.88	−3.94	−3.61	−0.66
358.15	61.83	−1.17	−3.30	−2.72	−0.16
363.15	62.55	−0.74	−2.96	−2.18	0.03
368.15	62.99	−0.77	−3.09	−2.11	−0.28
373.15	63.43	−0.79	−3.21	−2.04	−0.62
378.15	64.15	−0.38	−2.90	−1.53	−0.56
383.15	65.46	0.93	−1.68	−0.14	0.37
388.15	66.18	1.30	−1.41	0.29	0.34
393.15	66.91	1.68	−1.15	0.72	0.28
398.15	67.93	2.46	−0.47	1.52	0.60
403.15	68.80	3.00	−0.05	2.09	0.67
408.15	69.38	3.13	−0.05	2.18	0.28
413.15	70.25	3.64	0.34	2.64	0.27
418.15	70.98	3.95	0.52	2.90	0.02
423.15	71.55	4.04	0.45	2.93	−0.48
428.15	72.43	4.52	0.80	3.37	−0.58

	Bondi eq	Sternling–Brown eq	Yuan–Stiel eq	empirical
mean dev[e]	1.97	2.09	2.55	0.35
max dev[f]	4.52	−3.98	−4.25	0.67

[a] Equation 22. [b] Equation 23. [c] Equation 24. [d] Equation 26. [e] ϵ = heat capacity deviation = $100(C_{p\mathrm{L,exptl}} - C_{p\mathrm{L,calcd}})/C_{p\mathrm{L,exptl}}$. [f] $100\sum_i(|C_{p\mathrm{L,exptl}} - C_{p\mathrm{L,calcd}}|/C_{p\mathrm{L,exptl}})_i/n$.

18). The various constant terms in eq 15 and 18 can be lumped together to give the following simplified Yen–Woods equation form

$$\rho_s = \sum_{j=0}^{4} b_j(1 - T_r)^{j/3} \tag{19}$$

where

$$b_j = \rho_c K_j \quad \text{for } j = 0, 1, ..., 4$$

with $K_0 = 1$. Values for the constants in eq 16 and 19 are given in Table XI corresponding to the results given in Tables IX and X.

The results in Tables IX–XI show that the empirical equation produces the lowest error when compared to the Yen–Woods equation results. The Yen–Woods equation yields errors of less than 4%, but this is reduced to less than 0.5% over the indicated temperature range when a reference density is used.

Ideal Gas Thermodynamic Properties. Table XII contains ideal gas enthalpy of formation $\Delta H_f°$, entropy $S°_{298}$, entropy of formation $\Delta S_f°$, Gibbs energy of formation $\Delta G_f°$, and heat capacity $C_p°$ at various temperatures for each aldehyde. These were developed by using Benson's group contribution method (*19*, *20*) where the various additive values were taken from the tables given by Reid et al (*6*). Correction terms to the ideal gas entropy $S°_{298}$ for symmetry, isomers, and alkane gauche interactions were also included. The $\Delta S_f°$ values were obtained from the estimated values of $S°_{298}$ for each compound and the $S°_{298}$ values for the elements given in Stull et al. (*21*) using the elemental synthesis reaction. Values for the ideal gas free energy of formation at T = 298 K were calculated from the estimated values of $\Delta H_f°$ and $\Delta S_f°$ by using the following thermodynamic relationship

$$\Delta G_f° = \Delta H_f° - T\Delta S_f° \tag{20}$$

Table XV. Liquid Heat Capacities of 3,4-Dimethylpentanal

obsd		ϵ[e]			
T, K	C_{pL}, cal mol^{-1} K^{-1}	Bondi eq[a]	Sternling–Brown eq[b]	Yuan–Stiel eq[c]	empirical[d]
323.15	56.31	-4.13	-5.49	-6.84	0.25
328.15	56.49	-4.61	-6.03	-7.10	0.31
333.15	56.31	-5.77	-7.26	-8.07	-0.37
338.15	56.58	-6.08	-7.63	-8.18	-0.34
343.15	56.76	-6.56	-8.18	-8.48	-0.56
348.15	57.48	-6.04	-7.73	-7.76	0.06
353.15	58.02	-5.86	-7.62	-7.43	0.27
358.15	58.37	-6.02	-7.87	-7.42	0.06
363.15	59.28	-5.20	-7.12	-6.47	0.69
368.15	59.63	-5.36	-7.38	-6.54	0.31
373.15	60.17	-5.21	-7.32	-6.28	0.14
378.15	60.70	-5.06	-7.27	-6.05	-0.11
383.15	61.33	-4.76	-7.07	-5.65	-0.30
388.15	62.05	-4.31	-6.72	-5.15	-0.42
393.15	62.86	-3.73	-6.24	-4.51	-0.48
398.15	63.93	-2.73	-5.34	-3.48	-0.21
403.15	64.56	-2.48	-5.20	-3.20	-0.72
408.15	66.26	-0.58	-3.38	-1.27	0.33
413.15	67.79	0.97	-1.91	0.23	1.01
418.15	68.78	1.67	-1.33	0.89	0.79
423.15	69.68	2.23	-0.88	1.41	0.38
428.15	69.85	1.76	-1.51	0.88	-1.14

	Bondi eq	Sternling–Brown eq	Yuan–Stiel eq	empirical
mean dev[e]	4.14	5.75	5.15	0.42
max dev[f]	-6.56	-8.18	-8.48	-1.14

[a] Equation 22. [b] Equation 23. [c] Equation 24. [d] Equation 26. [e] ϵ = heat capacity deviation = $100(C_{pL,\mathrm{exptl}} - C_{pL,\mathrm{calcd}})/C_{pL,\mathrm{expt}}$. [f] $100\sum_i(|C_{pL,\mathrm{exptl}} - C_{pL,\mathrm{calcd}}|/C_{pL,\mathrm{exptl}})_i/n$.

Table XVI. Empirical Liquid Heat Capacity Equation Constants

compd	liq heat capacity polynomial const[a]
3-methylhexanal	$c_0 = 0.8915144 \times 10^2$ $c_1 = -0.2700479$ $c_2 = 0.5418013 \times 10^{-3}$
prms[b]	0.4165
3,4-dimethylpentanal	$c_0 = 0.1615298 \times 10^3$ $c_1 = -0.6761820$ $c_2 = 0.1083506 \times 10^{-2}$
prms[b]	0.5123

[a] Equation 26. [b] Percent root mean square deviation defined by $100[\sum_i((C_{pL,\mathrm{exptl}} - C_{pL,\mathrm{calcd}})/C_{pL,\mathrm{expt}})_i^2/n]^{1/2}$.

The derived ideal gas heat capacity data given in Table XII were used to determine the constants in the following polynomial equation by least squares

$$C_p{}^\circ = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4/T^2 \qquad (21)$$

Values for the constants a_0, a_1, ..., a_4 are given in Table XIII along with the percent root mean square deviation which never exceed 4.7×10^{-4}%. Other heat capacity equation forms can also be used, but eq 21 has been shown through prior experience to give excellent results.

Liquid Heat Capacities. Tables XIV and XV give the experimental liquid heat capacity data for each compound and the deviations obtained when various corresponding-states-based equations and an empirical equation form were used to interpret the results. The corresponding-states equations used here included the Rowlinson correlation (*22*) as modified by Bondi (*23*), the Sternling and Brown correlation (*6*), and the nonpolar liquid form of the Yuan and Stiel correlation (*24*). These equations provide estimates of the liquid heat capacity and require the ideal gas heat capacity $C_p{}^\circ$, the critical temperature T_c, and the acentric factor ω as input parameters. The particular equation forms used here are given below:

Rowlinson correlation

$$C_{pL} = C_p{}^\circ + R\{2.56 + 0.436(1 - T_r)^{-1} + \omega[2.91 + 4.28(1 - T_r)^{1/3}T_r^{-1} + 0.296(1 - T_r)^{-1}]\} \qquad (22)$$

Sternling and Brown correlation

$$C_{pL} = C_p{}^\circ + R\{(0.5 + 2.2\omega)[3.67 + 11.64(1 - T_r)^4 + 0.634(1 - T_r)^{-1}]\} \qquad (23)$$

Yuan and Stiel correlation

$$C_{pL} = C_{\sigma L} + R\{(1 + \omega)^{0.85}\ [\exp(-0.7074 - 31.014T_r + 34.361T_r^2)]\} \qquad (24)$$

where

$$C_{\sigma L} = C_p{}^\circ + (\Delta C_\sigma)^{(0)} + \omega(\Delta C_\sigma)^{(1)} \qquad (25)$$

The deviation functions $(\Delta C_\sigma)^{(0)}$ and $(\Delta C_\sigma)^{(1)}$ in eq 25 are tabulated in Reid et al. (*6*) as a function of reduced temperature. Evaluation of various empirical equation forms for goodness of fit showed that the following three-constant equation provided good results

$$C_{pL} = c_0 + c_1T + c_2T^2 \qquad (26)$$

The empirical constants c_0, c_1, and c_2 in eq 26 are given in Table XVI.

The results in Tables XIV–XVI show that the various corresponding-states correlations generally overpredict the liquid heat capacity since the mean deviations are negative except for the case where the Bondi equation is applied to 3-methylhexanal. This equation has the smallest mean deviation among the various corresponding-state equations, while the empirical equation has the least error of all four equations that were tested. Although the empirical equation results are superior to the others, those based on the corresponding-state methods can be readily applied to novel compounds by using derived quantities with errors that are acceptable for engineering design estimates.

Conclusions

Hydroformylation of selected C_6 hexenes using a homogeneous rhodium–phosphine ligand catalyst is an efficient method for preparing C_7 aldehydes in high selectivity. This is especially attractive for applications such as the one encountered here where experimental property measurements for a particular aldehyde are required and high purity is important.

The normal boiling point for the C_7 aldehydes in this study could be reliably estimated by using a combination of Fedor's method for the critical temperature and Lydersen's method for the reduced boiling temperature, both of which require tabulated group contribution structural data. It was shown that the relative errors between experimental and group contribution based values for the normal boiling point had maximum relative errors of 1.72%. In addition, the group contribution method gives correct trends with regard to the effect of branching on the normal boiling point for the aldehyde isomers.

Of the various vapor pressure equations that were tested, the Miller equation gave the lowest errors between experimental and predicted values when compared to the Antoine equation and the Riedel–Plank–Miller equations. The form of the Miller equation is similar to the Antoine equation, except it has an additional adjustable parameter which may explain its ability to provide lower errors. The Riedel–Plank–Miller equation gave the largest errors, but these were reduced to an acceptable magnitude when the critical pressure and critical temperature were adjusted to fit the data.

An attempt to obtain the critical properties and acentric factor by extrapolation of the vapor pressure data using corresponding-states equations yielded a good fit of the data, but the values for the critical properties were not consistent. Further investigation is required to assess the reliability of group contribution methods for determine of the critical properties for aldehydes.

The Yen–Woods equation for prediction of saturated liquid density gave errors of less than 4% when compared to experimental values over the range of 25–100 °C. The only parameters needed to evaluate this equation are the critical properties which can be obtained from a structural group contribution approach such as Lydersen's method. When a single reference temperature density datum point was available, the maximum errors were reduced to less than 0.5% over the above temperature range. An empirical equation that was linear in temperature with two adjustable parameters produced absolute maximum errors of less than 0.15%, but this equation is not general and can only be applied to a particular compound.

Ideal gas heat capacities derived from the group contribution method of Benson varied from 41 cal mol^{-1} K^{-1} to 89 cal mol^{-1} K^{-1} over the temperature range of 300–1000 K for both C_7 aldehydes. These data were fitted to temperature polynomial with five adjustable parameters which resulted in root mean square errors of less than 5×10^{-4}%.

Ideal gas enthalpies of formation for both 3-methylhexanal and 3,4-dimethylpentanal are exothermic with typical values being about −65 kcal mol^{-1} at 298.15 K.

Liquid heat capacities for both 3-methylheptanal and 3,4-dimethylheptanal were predicted by the corresponding-states correlations of Rowlinson, Sternling and Brown, and Yuan and Stiel with an absolute value of the maximum error of less than 8.5% when compared to experimental data over the temperature range of 50–155 °C. An empirical equation that was a quadratic equation in temperature with three adjustable constants produced errors of less than 1%, but it cannot be applied to compounds where data are not yet available. The Bondi correlation generally gives smaller absolute errors than the above correlations and is the preferred method when experimental data are not available.

Acknowledgment

We acknowledge George F. Schaefer, Frank J. Doering, Mark Trampe, and Don Willis for their assistance in the experimental portion of this work. In addition, we acknowledge the Physical Sciences Center for making the experimental physical property measurements and thermal stability measurements.

Glossary

a_j	ideal gas heat capacity polynomial constants in eq 21
A	liquid density constant in eq 16
A_a	Antoine vapor pressure equation constant in eq 4
A_m	Miller vapor pressure equation constant in eq 3
b_j	Yen–Woods equation constants in eq 19
B	liquid density constant in eq 16
B_a	Antoine vapor pressure equation constant in eq 4
B_m	Miller vapor pressure equation constant in eq 3
c_j	empirical liquid heat capacity equation constants in eq 26
C_a	Antoine vapor pressure equation constant in eq 4
C_m	Miller vapor pressure equation constant in eq 3
$C_p{}^\circ$	ideal gas heat capacity, cal mol^{-1} K^{-1}
C_{pL}	liquid heat capacity at constant pressure, cal mol^{-1} K^{-1}
$C_{\sigma L}$	saturated liquid heat capacity, cal mol^{-1} K^{-1}
D_a	Antoine vapor pressure equation constant defined by eq 7
D_m	Miller vapor pressure equation constant in eq 3
G	Riedel–Plank–Miller vapor pressure equation constant defined by eq 9
$\Delta G_f{}^\circ$	standard Gibbs free energy of formation defined by eq 20, cal mol^{-1}
h	Riedel–Plank–Miller vapor pressure equation constant defined by eq 8
$\Delta H_f{}^\circ$	standard enthalpy of formation, cal mol^{-1} K^{-1}
k	Riedel–Plank–Miller vapor pressure equation constant defined by eq 10
K_j	Yen–Woods saturated liquid density equation constant in eq 15
n	denotes the total number of points
P	vapor pressure, kPa
P_c	critical pressure, atm or kPa
P_r	reduced pressure in eq 11
R	ideal gas constant, J K^{-1} mol^{-1}
$S^\circ{}_{298}$	ideal gas entropy, cal mol^{-1} K^{-1}
$\Delta S_f{}^\circ$	standard entropy of formation, cal mol^{-1} K^{-1}
T	temperature, K
T_b	normal boiling temperature in eq 1, K
T_{br}	reduced normal boiling temperature in eq 1, dimensionless
T_c	critical temperature in eq 1, K
T_r	reduced temperature, T/T_c, dimensionless
$T_{r,ref}$	reduced temperature at the reference temperature, dimensionless
V_c	critical volume, cm^3 mol^{-1}
Z_c	critical compressibility, dimensionless
ϵ	percent deviation in Table I
ρ_c	critical density in eq 15, g cm^{-3}
$\rho_{s,ref}$	saturated liquid density at the reference temperature in eq 18, g cm^{-3}
ρ_s	saturated liquid density at the solution temperature T in eq 15, g cm^{-3}
ω	acentric factor defined by eq 12, dimensionless

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Received for review December 19, 1985. Accepted December 16, 1986.