Application of correlation-gas chromatography to evaluate the vaporization enthalpy of a component in an equilibrium mixture

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Abstract

The vaporization enthalpies and vapor pressures of acetoin, ethyl 3-hydroxybutyrate and ethyl 3-hydroxyhexanoate, found in a variety of foods and flavors, are evaluated at $T = 298.15$ K using correlation-gas chromatography; values of (48.7 ± 0.4), (55.9 ± 0.6) and (61.9 ± 0.6) kJ mol^{-1}, respectively, were obtained. These values are in good agreement with estimated values. Vapor pressures of the standards as a function of temperature were also used to calculate vapor pressures of the target compounds and all resulting data were fit to second order polynomials. These polynomials were then used to predict boiling temperatures of both standards and target substances. Agreement with experimental boiling temperatures was generally within 10 K suggesting that vapor pressures are accurate to within a factor of two. Acetoin exists as an equilibrium mixture of monomer and dimer. This report provides an example of the utility of using correlation-gas chromatography to obtain thermochemical data on an impure material.
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1. Introduction

Correlation-gas chromatography (GC) has been used to evaluate the vaporization enthalpies of pure materials as well complex mixtures [1,2]. Occasionally, a material exists primarily in equilibrium between different species. Under these circumstances, evaluation of the vaporization enthalpy of the pure component or components by traditional methods, such as calorimetry or mass effusion, is not possible. We would like to illustrate the use of correlation-gas chromatography to evaluate the vaporization enthalpy and vapor pressure of one of the components in such an equilibrium mixture.

Acetoin (3-hydroxy-2-butanone or acetylmethylcarbinol) is commercially available as a mixture of a liquid monomer and a crystalline dimer as illustrated in Fig. 1. It is found in

a variety of foods and is an important constituent of various flavors [3–7]. Solid dimer is converted to liquid monomer on melting, dissolution or distillation. It gradually reverts to dimer on standing and it is easily oxidized under atmospheric conditions to form diacetyl [8]. Some commercial sources supply acetoin as the dimer (Aldrich, mp 90–91 °C) or as a mixture of the monomer and the dimer (Lancaster). Since the monomer contains an asymmetric center and two new asymmetric centers are generated upon formation of the dimer, a total of four asymmetric centers are present. This result in formation of seven possible diasteriomers, some of which exists as *dl* pairs. The different diasteriomers are illustrated in Fig. 2. Compounds 1 and 2 in this figure contain a center of symmetry and are *meso* forms. The remainder exist as *dl* pairs. Although not all of the forms may be present concurrently, different melting points reported for the dimer, 85 and 95 °C, suggests that a number of them are readily accessible. The crystal structure of diasteriomer 1 has been determined [9]. The structure was not correlated to any physical property such as melting temperature that would identify the particular diasteriomer associated with this structure.

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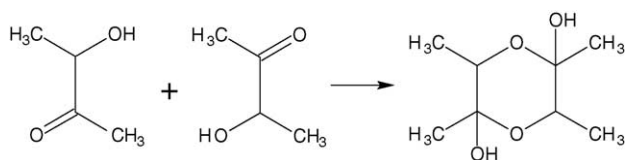
Fig. 1. Dimerization reaction of acetoin.

The present study reports the vaporization enthalpy and vapor pressure of acetoin (as the monomer), ethyl 3-hydroxybutyrate and ethyl 3-hydroxyhexanoate by correlation-GC. GC in conjunction with mass spectrometry has been widely used to determine the presence of the acetoin in natural samples [3–7]. Ethyl 3-hydroxybutyrate [10–13] and ethyl 3-hydroxyhexanoate [14–18] are also found in a variety of natural substances such as oranges and in wines, and as such are constituents of natural flavors.

2. Experimental

The compounds studied were all obtained from commercial vendors in high chemical purity (>98%). The gas chromatograph used to measure retention times was an HP 5980 Series II instrument equipped with a split–splitless capillary injection port and a FID detector. A split ratio of approximately 50:1 was used. A 30 m RTX-5 capillary column was used for the analyses. The retention times were recorded to three significant figures following the decimal point on an HP 3356 Series II integrator. The solvent used was methylene chloride. At the lower temperatures of these experiments, 90–120 °C, CH_2Cl_2 was retained. Methane was bubbled into the solution just prior to injection and was used as the non-retained reference. The retention time of methane was

used to determine the dead volume of the column. Adjusted retention times, t_a, were calculated by subtracting the retention time of methane from the retention time recorded for each analyte. Column temperatures were controlled by the instrument and monitored using a Fluke 51 K/J thermometer. All correlation-gas chromatography experiments were performed in duplicate to confirm reproducibility. The results of only one experiment are reported below. GC–MS experiments were performed on an HP 5988 A instrument. The methods and procedures used to determine the enthalpy of vaporization and vapor pressures have been described in the literature [1,19].

The acetoin sample used in our experiments contained a significant amount of solid indicating the presence of dimer. Injection in GC of the liquid revealed the presence of several compounds (the first with a short retention time of approximately 1.6 min at 90 °C and the others at approximately 8 min). GC–MS experiments confirmed that the compound with the shortest retention time corresponds to acetoin and that the compounds with longer retention times are the dimeric forms. Identification was assisted by comparison to the mass spectra available at the NIST webbook (webbook.nist.gov/chemistry).

3. Results

A GC trace of our sample of acetoin is shown in Fig. 3. On this column, the dimers appear as broad peaks suggesting that they are not clearly resolved. The acetoin peak, on the other hand, is very sharp and well resolved. This is significant since the sharpness suggests that once the sample leaves the injector, the monomer–dimer equilibrium is interrupted and that no equilibration occurs on the stationary phase of
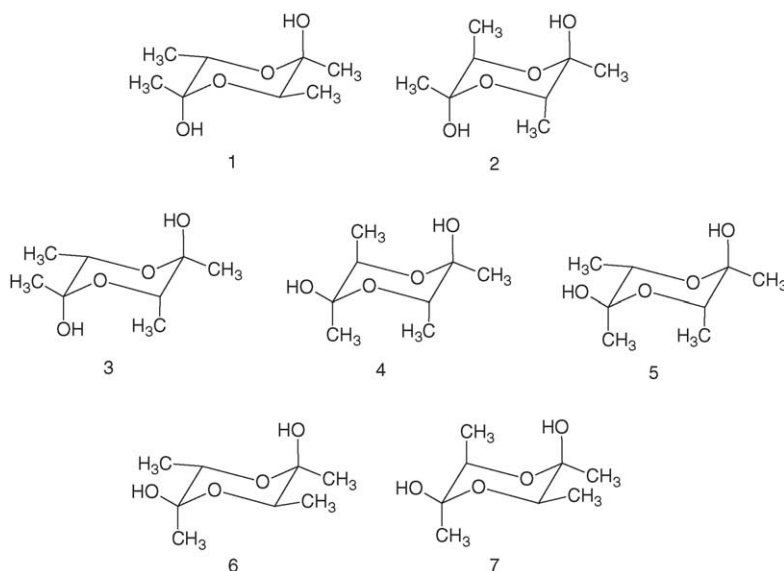

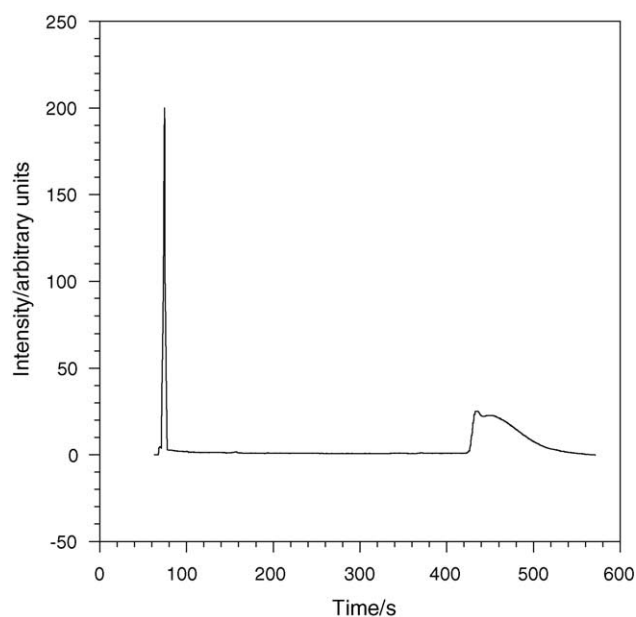Fig. 2. Diastereomers of acetoin dimer.

Fig. 3. A GC trace of 3-hydroxy-2-butanone and its corresponding dimers at $T = 90\,^{\circ}C$. The solvent peak is not shown.

the column, at least under the dilute conditions used in our experiments.

Correlation-gas chromatography is not a direct method for determining vaporization enthalpies. What is determined directly is the enthalpy of transfer from the condensed phase of the column to the gas phase, $\Delta_{sln}^{g}H_{m}$. A value of $\Delta_{sln}^{g}H_{m}$

is obtained by plotting $\ln(1/t_{a})$, where t_{a} represents the time each analyte spends on the column, against reciprocal temperature, K^{-1}. The reciprocal of t_{a} is proportional to the vapor pressure of each analyte on the stationary phase of the column at a particular temperature. Enthalpies of transfer measured experimentally are correlated to known vaporization enthalpies measured by some other means. The vaporization enthalpy of the target is obtained from the correlation equation. Selection of the reference compounds is crucial in the evaluation. Generally, reference compounds are chosen with the same type and number of functional groups as the target compound. Some flexibility is possible in certain cases where it has been demonstrated empirically that functional group substitution still provides suitable correlations. For example, good correlations have previously been obtained when an ester group is substituted for a ketone as in this study [20]. A rationale for this has recently been reported [21].

The reference compounds chosen for this study include methyl glycolate, ethyl lactate, 4-hydroxy-4-methyl-2-pentanone and methyl salicylate. The target compounds include acetoin, ethyl 3-hydroxybutyrate and ethyl 3-hydroxyhexanoate. Methyl glycolate and acetoin have similar retention times at the temperatures of this study and could not be used in the same GC experiments. In view of the relatively few standards available, methyl glycolate along with ethyl lactate, 4-hydroxy-4-methyl-2-pentanone and methyl salicyclate were used in the evaluation of the vaporization enthalpies and vapor pressures of ethyl 3-hydroxybutyrate

Table 1
Summary of literature values[a]

Compound	$\Delta_{l}^{g}H_{m}(T_{m})$ (kJ mol^{-1})	Range (K)	T_{m} (K)	$\Delta_{l}^{g}H_{m}$ (298.15K) (kJ mol^{-1})	Mean value $\Delta_{l}^{g}H_{m}$ (298.15K) (kJ mol^{-1})	Reference
Methyl glycolate	48.4	327–60	343	51.0	48.8 ± 2.4	[22]
	45.5	298–348	323	47.0		[23]
	46.2	318–355	337	48.5		[24]
Acetoin	38.4		288	37.8[b]		[23]
	2.67	283–313	298	2.67[b,c]		[28]
	40.4 ± 1.7	372–405	389	46.0 ± 2.2[b]		[8]
Ethyl lactate	48.2	320–355	338	51.1	52.5 ± 3.0	[23]
	49.4	340–375	339	53.8		[23]
4-Hydroxy-4-methyl-2-pentanone	49.8	320–360	340	53.0	52.3 ± 1.4	[24]
	48.0	315–375	345	51.5		[25]
	52.1[b,d]					[26]
Methyl salicylate	59.9	327–357	342	63.4	62.0 ± 1.8	[23]
	58.7	329–359	344	62.4		[23]
	56.9	288–318	303	57.3[b]		[23]
	55.8	327–383	355	60.3		[24]

[a] Vaporization enthalpies were adjusted to 298.15 K using Eq. (2) and the following estimated heat capacities: C_{pl} (methyl glycolate) = 183.1 J mol^{-1} K^{-1}, C_{pl} (acetoin) = 196.8 J mol^{-1} K^{-1}, C_{pl} (ethyl lactate) = 240.4 J mol^{-1} K^{-1}, C_{pl} (4-hydroxy-4-methyl-2-pentanone) = 255.2 J mol^{-1} K^{-1}, C_{pl} (methyl salicylate) = 269.0 J·mol^{-1} K^{-1}[27].

[b] Value not used.

[c] The plot of $\ln(p/kPa)$ vs. $1/T$ is not linear.

[d] Reference temperature not given.

Table 2
Retention times at different temperatures

	$t_{\min}$ (K)						
	363.1	368.2	373.3	378.4	383.5	388.6	393.7
Run 1							
Methane	1.061	1.072	1.085	1.093	1.100	1.111	1.120
Methyl glycolate	1.536	1.491	1.457	1.423	1.395	1.375	1.358
Ethyl lactate	2.125	1.990	1.881	1.787	1.708	1.646	1.593
4-Hydroxy-4-methyl-2-pentanone	2.380	2.207	2.068	1.948	1.848	1.768	1.700
Ethyl 3-hydroxybutyrate	3.528	3.156	2.856	2.607	2.401	2.236	2.098
Ethyl 3-hydroxyhexanoate	10.382	8.675	7.330	6.256	5.398	4.715	4.163
Methyl salicylate	15.743	13.045	10.916	9.219	7.859	6.775	5.897
Run 2							
Methane	1.105	1.115	1.120	1.127	1.138	1.143	1.151
Acetoin	1.587	1.540	1.495	1.460	1.435	1.408	1.390
Ethyl lactate	2.135	2.004	1.890	1.798	1.725	1.659	1.607
4-Hydroxy-4-methyl-2-pentanone	2.392	2.223	2.078	1.960	1.865	1.781	1.715
Ethyl 3-hydroxy butyrate	3.545	3.177	2.872	2.623	2.423	2.253	2.115
Ethyl 3-hydroxy hexanoate	10.435	8.729	7.376	6.300	5.443	4.753	4.198
Methyl salicylate	15.820	13.129	10.987	9.283	7.922	6.828	5.946

and ethyl 3-hydroxyhexanoate. These values were then used as substitutes for methyl glycolate in run 2 along with ethyl lactate, 4-hydroxy-4-methyl-2-pentanone and methyl salicylate to evaluate the vaporization enthalpy of acetoin.

Literature vaporization enthalpies of the standards are reported in Table 1 [8,22–26,28]. In cases where experimental vapor pressure data were available, vaporization enthalpies were calculated directly from the data over the temperature range indicated in the table. Values were also calculated from the Antoine equation, Eq. (1), if experimental data was not available.

$$\log(p) = A - \frac{B}{(T + C)} \tag{1}$$

The vaporization enthalpies were adjusted to $T = 298.15$ K using Eq. (2):

$$\Delta_l^g H_m(298.15\,\text{K})/\text{kJ mol}^{-1} = \Delta_l^g H_m(T_m) + \frac{[(10.58 + 0.26 C_{pl\,m})(T_m - 298.15)]}{1000} \tag{2}$$

where $C_{pl\,m}$, refers to the molar heat capacity of the liquid. The $C_{pl\,m}$, values used in the temperature adjustments are summarized at the bottom of Table 1 all were estimated by group additivity [27]. Agreement between different reported values is generally quite good. In a few cases, the agreement is poorer and these values were not used in generating the mean. The mean value was used as the reference value in our

Table 3
A summary of calculated values obtained by correlation-gas chromatography

Compound	Slope	Intercept	$\Delta_{sln}^g H_m$ (378 K) kJ mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ mol^{-1} (literature)	$\Delta_l^g H_m$ (298.15 K) kJ mol^{-1} (calculated)
Run 1					
Methyl glycolate	−3233.1	9.6515	26.88	48.8	48.7 ± 0.6
Ethyl lactate	−3786.5	10.371	31.48	52.5	52.3 ± 0.6
4-Hydroxy-4-methyl-2-pentanone	−3836.6	10.294	31.90	52.3	52.7 ± 0.6
Ethyl 3-hydroxybutyrate	−4323.1	11.008	35.94		55.9 ± 0.6
Ethyl 3-hydroxyhexanoate	−5232.1	12.183	43.50		61.8 ± 0.6
Methyl salicylate	−5247.8	11.774	43.63	62.0	61.9 ± 0.6

$$\Delta_l^g H_m(298.15)/\text{kJ mol}^{-1} = (0.792 \pm 0.024)\Delta_{sln}^g H_m(378\,\text{K}) + (27.40 \pm 0.30) \quad r^2 = 0.998 \tag{3}$$

Run 2					
Acetoin	−3286.7	9.784	27.32		48.7 ± 0.4
Ethyl lactate	−3809.9	10.466	31.67	52.5	52.3 ± 0.4
4-Hydroxy-4-methyl-2-pentanone	−3860.0	10.382	32.09	52.3	52.6 ± 0.4
Ethyl 3-hydroxybutyrate	−4340.3	11.066	36.08	55.9	55.9 ± 0.4
Ethyl 3-hydroxyhexanoate	−5230.4	12.177	43.48	62.0	61.9 ± 0.4
Methyl salicylate	−5241.8	11.752	43.58	62.0	62.0 ± 0.4

$$\Delta_l^g H_m(298.15\,\text{K})/\text{kJ mol}^{-1} = (0.818 \pm 0.019)\Delta_{sln}^g H_m(378\,\text{K}) + (26.33 \pm 0.22) \quad r^2 = 0.998 \tag{4}$$

Table 4
Summary of $\Delta_l^g H_m$ (298.15 K) values; all in kJ mol^{-1}

Compound	Run 1		Run 2		Mean
Methyl glycolate	48.7 ± 0.6	48.8 ± 0.5			48.8 ± 0.6
Acetoin			48.7 ± 0.4	48.6 ± 0.4	48.7 ± 0.4
Ethyl lactate	52.3 ± 0.6	52.2 ± 0.5	52.2 ± 0.4	52.3 ± 0.4	52.3 ± 0.6
4-Hydroxy-4-methyl-2-pentanone	52.7 ± 0.6	52.5 ± 0.5	52.6 ± 0.4	52.6 ± 0.4	52.6 ± 0.6
Ethyl 3-hydroxybutyrate	55.9 ± 0.6	55.8 ± 0.5			55.9 ± 0.6[a]
Ethyl 3-hydroxyhexanoate	61.8 ± 0.6	62.0 ± 0.5			61.9 ± 0.6[a]
Methyl salicylate	61.9 ± 0.6	62.1 ± 0.5	62.0 ± 0.4	62.1 ± 0.4	62.1 ± 0.6

[a] Value used as a reference value in run 2.

correlations. The uncertainty reflects two standard deviations of the mean. Also included in this table are earlier reports of the vaporization enthalpy of acetoin [8,23,28]. These values are quite different and were not used as standards because of the propensity of the acetoin to dimerize and oxidize; they are included for comparison purposes only.

The retention times for two different runs are reported in Table 2. Also as noted above, only one set of duplicate runs is reported here. Plots of $\ln(1/t_a)$ verses $1/T$ resulted in straight lines characterized by the slopes and intercepts reported in Table 3. The correlation coefficient, r^2, exceeded 0.99 in all cases. The correlation between enthalpies of transfer $\Delta_{sln}^g H_m(T_m)$ measured at the mean temperature, T_m, and vaporization enthalpies at $T = 298.15$ K resulted in Eqs. (3) and (4) given beneath each respective correlation in Table 3. This resulted in the vaporization enthalpies reported in the last column of Table 3. The uncertainty reported in this column reflects two standard deviations associated with the intercept of each correlation equation. Duplication of run 1 resulted in mean values of (55.9 ± 0.6) and (61.9 ± 0.6) kJ mol^{-1} for ethyl 3-hydroxybutyrate and ethyl 3-hydroxyhexanoate, respectively. These values, reported in the last column of Table 4, were then used as standards in run 2 to evaluate the vaporization enthalpy of acetoin.

A summary of all the results obtained is given in Table 4. The precision of our results is generally within ±1 kJ mol^{-1}. The accuracy of the values of acetoin, ethyl 3-hydroxybutyrate and ethyl 3-hydroxyhexanoate is probably similar in magnitude to the uncertainty of our standards reported in the last column of Table 1, about ±2 kJ mol^{-1}. Comparison of the literature values of acetoin (Table 1) with the results obtained in this study is in reasonably good agreement with the results of Efron and Blom [8]. The difference of 2.7 kJ mol^{-1} is just slightly larger than the estimates of the uncertainty of our results but well within the uncertainty associated with the combined results.

The vaporization enthalpies evaluated for acetoin (48.7 ± 0.4), ethyl 3-hydroxybutanoate (55.9 ± 0.6) and ethyl 3-hydroxyhexanoate (61.8 ± 0.6) kJ mol^{-1}, can be compared to values estimated using Eq. (5) [29]:

$$\Delta_l^g H_m(298.15 \text{ K})/\text{kJ mol}^{-1}$$

$$= 4.69 n_C + \sum_i F_i b_i + 3.0 + C. \tag{5}$$

The term n_C refers to the number of non-quaternary carbon atoms, F_i depends on the substitution pattern of the carbon to which the functional group is attached, b_i the group value of the functional group and C is an additional correction term that corrects for various structural factors, in these instances, the presence of intramolecular hydrogen bonding in 5 and 6 membered rings (−7.6). For acetoin, there are four carbons and two functional groups. The carbonyl, $b_i = 10.5$, is attached to a primary sp^3 carbon (1.62) and a 1,1-geminally substituted tertiary sp^3 hybridized carbon (0.78), $F_i = (1.62 + 0.78)/2$. The hydroxyl group, $b_i = 29.4$ is also attached to a 1,1-geminally substituted tertiary sp^3 hybridized carbon, $F_i = 0.78$. The estimated values of 49.7 are in good agreement with the value, (48.7 ± 0.4) kJ mol^{-1}, obtained by correlation-gas chromatography. Ethyl 3-hydroxybutanoate and ethyl 3-hydroxyhexanoate are estimated similarly. The substitution and hybridization pattern of the carbons to which both ends of the ester groups are attached are secondary sp^3 carbons (1.08), $F_i = (1.08 + 1.08)/2$. The hydroxyl group in both compounds is attached to a tertiary sp^3 carbon, $F_i = 0.6$. Both compounds have intramolecular hydrogen bond corrections, −7.6. This results in estimated vaporization enthalpies of 52.5 and 62.9 kJ mol^{-1} for ethyl 3-hydroxybutanoate and ethyl 3-hydroxyhexanoate, respectively. The comparison with the values obtained by correlation-gas chromatography, (55.9 ± 0.6) and (61.9 ± 0.6) kJ mol^{-1}, respectively, agree quite well.

In addition to providing vaporization enthalpies, correlation-gas chromatography is also capable of providing vapor pressures as well, provided the vapor pressures of the standards are available [1]. As with vaporization enthalpies, the quality of the vapor pressures obtained depends to a large extent on the quality of the data available for the standards. The protocol for obtaining vapor pressures relies on the correlation observed between experimental values of $\ln(p/\text{kPa})$, where p refers to the vapor pressure of the standards and $\ln(1/t_a)$ calculated from plots of $\ln(1/t_a)$ verses $1/T$, at the temperature in question [1].

To evaluate the vapor pressures of acetoin, ethyl 3-hydroxybutyrate and ethyl 3-hydroxyhexanoate, the following protocol was followed. Values of the natural logarithm of vapor pressure, $\ln(p/\text{kPa})$, calculated from Antoine constants (or from experimental vapor pressure data from the literature) were correlated against $\ln(1/t_a)$ calculated from

Table 5
Antoine constants (A, B, C) and constants of Eq. (6) (A′, B′ and C′), used in calculating literature vapor pressures (kPa)

A	B	C	A′	B′	C′	Temperature range/K
Methyl glycolate						
			−233028	−4223.3	15.84	283–425[a]
6.49799	1578.06	−71.9043				326–405[b]
7.59063	2369.19	−0.58				282–425[c]
4-Hydroxy-4-methyl-2-pentanone						
			−283108	−4305	15.823	295–441[a]
8.5552	2482.93					301–388[d]
Methyl salicylate						
			−631782	−3183.9	13.604	327–496[a]
5.91298	1543.5	−101.547				327–497[c]
6.03559	1620.399	−93.687				329–496[c]
Ethyl lactate						
6.60606	1673.8	−62.21				308–426[c]
6.2975	1441.066	−90.17				324–427[c]

[a] Reference [24].
[b] Reference [22].
[c] Reference [23].
[d] Reference [25].

the slopes and intercepts of the equations reported in the second and third columns of Table 3 over the temperature range, $T = 298.15–423$ K, at 20 K intervals. Experimental vapor pressure data from the literature were first fit to a second order polynomial of the following form:

$$\ln(p) = A'\left(\frac{1}{T}\right)^2 + B'\left(\frac{1}{T}\right) + C' \qquad (6)$$

Values of $\ln(p)$ at the temperatures of interest were then calculated using this equation. The Antoine constants, the constants of Eq. (6), and the range of temperatures to which they are applicable are reported in Table 5.

Two separate sets of correlations were performed, each associated with either the equations reported for run 1 or run 2 in Table 3. The correlations of $\ln(p/\text{kPa})$ versus $\ln(1/t_a)$ associated with run 1 included methyl glycolate, 4-hydroxy-4-methyl-2-pentanone and methyl salicylate as standards. Ethyl lactate was not used as a standard in these correlations, since it did not correlate well with the other three compounds. Correlation coefficients (r^2) of 0.98 or better were obtained at each temperature interval. Ethyl lactate, as well as ethyl 3-hydroxybutyrate and ethyl 3-hydroxyhexanoate were treated as unknowns. The correlation equations relating $\ln(p/\text{kPa})$ to $\ln(1/t_a)$ of the standards were evaluated at 20 K temperature intervals. These equations (not reported) were then used in combination with the temperature dependence of $\ln(1/t_a)$ of the unknowns, ethyl lactate, ethyl 3-hydroxybutyrate and ethyl 3-hydroxyhexanoate, to calculate $\ln(p/\text{kPa})$ values for these substances at each temperature in the range. The resulting values of $\ln(p/\text{kPa})$ calculated from these correlation equations at each temperature were then plotted as a func-

Table 6
Coefficients of Eq. (6) and estimates of boiling temperatures (bp) obtained by correlating $\ln(p/\text{kPa})_{\text{expt}}$ with $\ln(1/t_a)$

Compound	A′	B′	C′	bp/K (calculated)	bp/K (literature)[a]
Run 1					
Methyl glycolate	−66993	−5051.3	16.908	424	422
Ethyl lactate	−254912	−4387.1	15.935	439	427
Ethyl 3-hydroxybutyrate	−450472	−3666.4	14.838	455	443
4-Hydroxy-4-methyl-2-pentanone	−303196	−4147.3	15.488	444	439
Ethyl 3-hydroxyhexanoate	−760647	−2566.7	13.222	323	333
Methyl salicyclate	−860453	−2005.2	12.111	498	495
Run 2					
Acetoin	−43374.7	−5063.3	16.813	424	422
Ethyl lactate	−254404	−4300.2	15.759	439	427
Ethyl 3-hydroxybutyrate	−489181	−3411.5	14.465	455	443
4-Hydroxy-4-methyl-2-pentanone	−308667	−4039.1	15.289	444	439
Ethyl 3-hydroxyhexanoate	−859433	−2051.1	12.549	323	333[b]
Methyl salicyclate	−964358	−1480.4	11.439	498	495

[a] Reference [30].
[b] Boiling temperature at 1 Torr [31].

Table 7
A comparison of extrapolated vapor pressures at 298.15 K calculated from the coefficients of Table 6 with those calculated from Table 5

	ln (p/kPa) (T = 298.15 K) this work		ln (p/kPa) (T = 298.15 K) literature				
	Run 1	Run 2	[24]	[23]	[22]	[25]	[8]
Methyl glycolate	−0.79		−0.95	−0.86	−1.1		
Acetoin		−0.66					0.00
Ethyl lactate	−1.65	−1.53		−1.12, −1.45			
Ethyl 3-hydroxybutyrate	−2.53	−2.48					
4-Hydroxy-4-methyl-2-pentanone	−1.83	−1.73	−1.80			−1.49	
Ethyl 3-hydroxyhexanoate	−3.94	−4.00					
Methyl salicyclate	−4.29	−4.38		−4.46	−4.36	−4.18	

tion of $1/T$ and fit to Eq. (6). The natural logarithm of vapor pressures of both standards and unknowns were fit.

The A', B' and C' coefficients that resulted from the first run are provided in Table 6. This process was repeated using all the compounds in run 2 as standards except acetoin in a second set of correlations. Values of ln(p/kPa) calculated from the A', B' and C' terms for ethyl lactate, ethyl 3-hydroxybutyrate and ethyl 3-hydroxyhexanoate generated in run 1 (Table 6) for were now also used as standards. These were combined with ln(p/kPa) values for 4-hydroxy-4-methyl-2-pentanone and methyl salicyclate generated from the constants in Table 5. The resulting sets of coefficients for Eq. (6) generated from the second run are also reported in Table 6. As a test of the quality of the equations resulting from these two correlations, the boiling temperatures of both standards and unknowns were predicted using ln(p/kPa) values generated from the constants reported in Table 6. The last two column of Table 6 compare these values to experimental ones. In most instances, the differences in boiling temperature is 10 K or less, suggesting that the vapor pressures obtained by correlation are within a factor two of the experimental values.

Table 7 compares ln(p/kPa) at $T = 298.15$ K obtained in this work with extrapolated literature values. Agreement is generally quite good. In addition, Fig. 4 compares the vapor pressures of acetoin reported by Efron and Blom [8] with those obtained using Eq. (6) and the coefficients for acetoin reported in run 2, Table 6. The literature vapor pressures are slightly larger than those calculated by Eq. (6) but well within the factor of two noted above.

4. Summary

Correlation-GC is used to evaluate the vaporization enthalpy and vapor pressure of a single pure component in the presence of an equilibrium mixture of several components. Such a direct evaluation is not possible by traditional methods such as calorimetry or mass effusion techniques. Vaporization enthalpies obtained for acetoin (48.7 ± 0.4), ethyl 3-hydroxybutanoate (55.9 ± 0.6) and ethyl 3-hydroxyhexanoate (61.8 ± 0.6) kJ mol^{-1} measured by correlation-gas chromatography can be compared to estimated values of 49.7, 52.5 and 61.9 kJ mol^{-1}, respectively. Equations to generate values of vapor pressure at different temperatures are also reported for acetoin, ethyl lactate, ethyl 3-hydroxybutanoate and ethyl 3-hydroxyhexanoate. Based on the normal boiling temperatures predicted by extrapolation, it is suggested these values are accurate to within a factor of two.
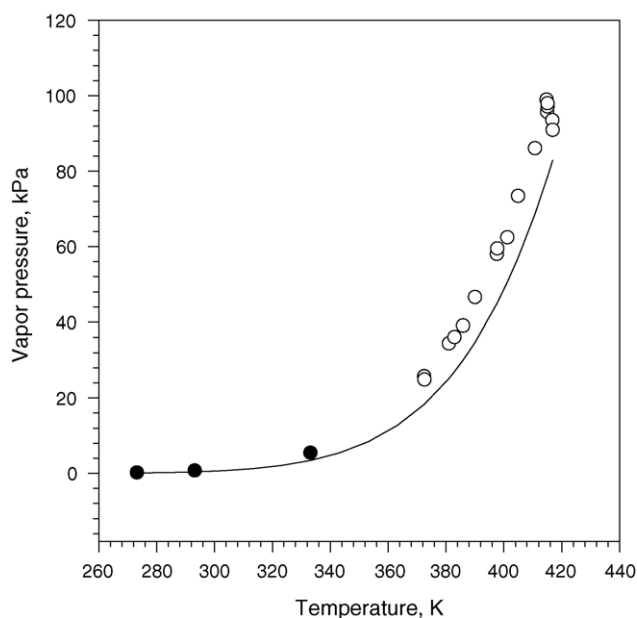
Fig. 4. The circles represent experimental vapor pressures reported for acetoin by Efron and Blom [8], the solid circles are extrapolated values. The line represents vapor pressures calculated with the aid of Eq. (6) and the coefficients in Table 6.

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