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Determination of Henry's Law Constants and Activity Coefficients at Infinite Dilution of Flavor Compounds in Water at 298 K with a Gas-Chromatographic Method

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Experimental results for Henry's law constants and activity coefficients at infinite dilution of the flavor compounds ethanol, propanol, acetone, 2-butanone, 2-pentanone, 2-hexanone, diacetyl, methyl sulfide, *cis*-4-heptenal, acetoin, and acetaldehyde in water are reported for a temperature of 298 K. The activity coefficients at infinite dilution were measured with the so-called relative stationary gas−liquid chromatographic method. This method makes use of a reference compound whose activity coefficient at infinite dilution in the solvent (in this case water, which is loaded onto a solid support in a packed chromatographic column) is known. This method is very useful for the determination of activity coefficients of infinite dilution of solutes in volatile solvents, which are difficult to measure in conventional gas−liquid chromatographic methods because of the stripping of the solvent from the column. The reproducibility of the measured values depends on the type of compound and is between ±1 and ±5 %. The choice of a value for the activity coefficient of the reference compounds can cause a systematic error of up to 3 %.

Introduction

In the food industry, the behavior of flavor compounds in products is an area of importance, especially in man-made structured food products. Food is, in general, a multiphase dispersion of a lipid-like phase and an aqueous phase. In the emulsified product, several other compounds are dissolved in the phases (e.g., proteins, sugars, and salts). For the taste sensation of the food products, flavor compounds are also included in the man-made products. The volatile flavor compounds are distributed (normally in very low concentrations) over the various phases in the product.

To describe the release of flavor compounds from food products, physical properties are important, such as activity coefficients at infinite dilution and vapor pressures. Water is usually the dominant component of food products, so we start with the determination of activity coefficients at infinite dilution of flavor compounds, which are of interest in the food industry, in water.

One of the fastest, most reliable, and most common techniques for measuring activity coefficients at infinite dilution is the dynamic gas−liquid chromatographic method. (See, for example, Palmer.[1]) This method is based on the influence of the solvent, which is absorbed on a solid support in a packed gas chromatographic column, on the retention of the solute. The solvent loading in the column has to be known accurately. This is a problem with volatile solvents such as water. Tassios[2] reported a method for the determination of volatilities at infinite dilution by a relative gas−liquid chromatographic method by the injection of the solvent into the column. Eckert et al.[3] measured with the conventional method and used a test solute with a known value for the activity coefficient at infinite dilution. With this test solute, the amount of solvent in the column was back calculated.

Orbey and Sandler[4] used the relative method for the determination of activity coefficients at infinite dilution for the solvent water. In this method, the column, which contains an inert solid support, was filled with water outside the gas chromatograph. After the column was placed and stabilized in the gas chromatograph, a mixture was injected with a reference compound whose activity coefficient at infinite dilution is known. The principle of the method is that during the measurements two (or more) compounds are simultaneously injected into the chromatographic column. From the ratio of the net retention times, the ratio of the vapor pressures of both compounds, and the activity coefficient at infinite dilution of the reference compound, the unknown activity coefficient can be calculated.

In this work, we used the basic principles proposed by Orbey and Sandler.[4] Furthermore, we introduce a correction factor for the evaporation of the solvent during the measurements.

Data Reduction

The generalized thermodynamic expression for the gas−liquid chromatographic method for the determination of the activity coefficient at infinite dilution (γ_2^∞) for the solute (2) in the solvent (1) is based on the work of Cruickshank et al.,[5]

$$\gamma_2^\infty = \frac{n_1 R T_{\mathrm{col}}}{V_{\mathrm{N}} P_2^{\mathrm{o}}} \exp \Phi_2 \tag{1}$$

where n_1 is the number of moles of solvent in the column, R is the gas constant, T_{col} is the temperature of the column,

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P_2^o is the vapor pressure of the solute at the column temperature, and Φ_2 is a correction factor for the nonideality of the phases. V_N is the retention volume given by

$$V_N = JQ\Delta t \frac{T_{col}}{T_f}\left(1 - \frac{P_{ow}}{P_{out}}\right) \qquad (2)$$

where J is the correction factor for the influence of the pressure drop along the column, Q is the flow rate of the carrier gas measured by a soap bubble flow meter, Δt is the net retention time of the solute (i.e., the retention time of the solute minus the retention time of an unretained component), T_f is the flow meter temperature, P_{ow} is the vapor pressure of water at T_f, and P_{out} is the pressure at the column outlet.

The correction factor for the nonideality of the phases for the solute (2) and the carrier gas (3) is given by

$$\Phi_2 = \frac{2B_{23} - V_2^\infty}{RT_{col}} JP_{out} - \frac{B_2 - V_2^o}{RT_{col}} P_2^o \qquad (3)$$

where B_{23} is the cross virial coefficient of the solute (2) and the carrier gas (3), B_2 is the second virial coefficient of the solute, V_2^o is the liquid molar volume of the pure solute, and V_2^∞ the partial molar volume of the solute in the solvent at infinite dilution, which is assumed to be equal to V_2^o.

Orbey and Sandler[4] suggested that for two solutes A and B, which run through the gas chromatographic column simultaneously, eq 1 can be used for the ratio of the activity coefficients at infinite dilution,

$$\frac{\gamma_A^\infty}{\gamma_B^\infty} = \frac{\Delta t_B P_B^o}{\Delta t_A P_A^o} \cdot \frac{\exp \Phi_A}{\exp \Phi_B} \qquad (4)$$

During the measurements, the solvent will be stripped from the column, which also can influence the flow and pressures. Therefore, the first three terms on the right-hand side of eq 1 will change during the GC runs. We introduce for this a correction factor $E(t_i^{IR})$, which is a function of the time of the experiment, within a series of measurements. The time of the experiment t_i^{IR} is here defined as the sum of the time of injection t_i^I and the time of retention of the compound t_i^R ($t_i^{IR} = t_i^I + t_i^R$). Equation 1 can be rewritten as

$$\gamma_i^\infty = E(t_i^{IR}) \frac{1}{\Delta t(t_i^{IR}) P_i^o} \exp \Phi_i \qquad (5)$$

where $\Delta t(t_i^{IR})$ is the net retention time of a component as function of the time of the experiment t_i^{IR}.

The correction factor $E(t_B^{IR})$ as function of the time of the experiment t_B^{IR} can be calculated with the results for the reference component (B)

$$E(t_B^{IR}) = \frac{(\gamma_B^\infty P_B^o)\Delta t(t_B^{IR})}{\exp \Phi_B} \qquad (6)$$

After regression analysis of the correction factor $E(t_B^{IR})$ as function of the time of the experiment t_B^{IR}, the correction factor $E(t_A^{IR})$ at the time of the experiment t_A^{IR} for solute A can be calculated. The activity coefficient at infinite dilution of solute A at time t_A^{IR} can be calculated with

$$\gamma_A^\infty = E(t_A^{IR}) \frac{1}{\Delta t(t_A^{IR}) P_A^o} \exp \Phi_A \qquad (7)$$

Table 1. Origin and Purity as Specified by the Supplier of the Components

component	CAS	origin	purity/% (on a mass basis)
methanol	[67-56-1]	Baker	>99.5 (GC)
ethanol	[64-17-5]	Baker	>99.8 (GC)
propanol	[71-23-8]	Baker	>99.0 (GC)
acetone	[67-64-1]	Baker	>99.5 (GC)
2-butanone	[78-93-3]	Merck	>99 (GC)
2-pentanone	[107-87-9]	Merck	>99 (GC)
2-hexanone	[591-78-6]	Fluka	~99 (GC)
diacetyl	[431-03-8]	Unilever	
methyl sulfide	[75-18-3]	Aldrich	99+
cis-4-heptenal	[6728-31-0]	Across	96+
acetoin	[513-86-0]	Aldrich	
acetaldehyde	[75-07-0]	Fluka	≥99.5 (GC)

If the vapor pressure of pure solute A is not known or not well known, then the Henry's law constants H_A of the solute can be calculated with

$$H_A = \gamma_A^\infty P_A^o = E(t_A^{IR}) \frac{1}{\Delta t(t_A^{IR})} \exp \Phi_A \qquad (8)$$

Experimental Section

Materials. The origin and purity of the solutes used in this work are given in Table 1. The components were used without any purification. The water used was common laboratory double-distilled water. Methane was used for the determination of the unretained retention time.

Apparatus and Procedure. For the determination of the activity coefficients at infinite dilution, we used a Hewlett-Packard 5890 series II gas chromatograph equipped with a Hewlett-Packard 7673 auto-sampler and a HP Kayak XA PC workstation with ChemStation software from Agilent Technologies.

The helium carrier gas (flow ±20 mL/min) is saturated with water in a presaturator prior to the injector by bubbling the gas through water. The water presaturator was placed in the oven of the gas chromatograph. The injector is a "packed column" inlet with a deactivated glass liner at a temperature of 175 °C. For the determination of the activity coefficient at infinite dilution, 0.5 μL of an aqueous solution of the compound and the reference compound was injected. The concentration of the compound in water was less than 0.1 vol. %. The amount of injected solute was adjusted by changing the concentration in the aqueous solution. The concentration was minimized for each experiment to obtain small and symmetrical peaks to guarantee infinite dilution conditions.

The column used was 45-cm-long Teflon tubing (PTFE, 1/8 in. o.d. × 0.098 in. i.d.). The column was filled with ±0.775 g Chromosorb 750 (Celite; purchased from Alltech, Deerfield, IL). The column was filled with water by placing one end in water and by applying suction at the other end. The column was placed in the gas chromatograph to remove the residual water in the column. The experiments can be started when roughly 0.5 g of water remains in the column. With less than 0.5 g of water, a stable baseline could be observed.

The temperature in the gas chromatographic oven was measured with a calibrated Pt-100 resistance thermometer coupled to a F25 precision thermometer from ASL (Automatic Systems Laboratories Ltd., Bradville, England). The

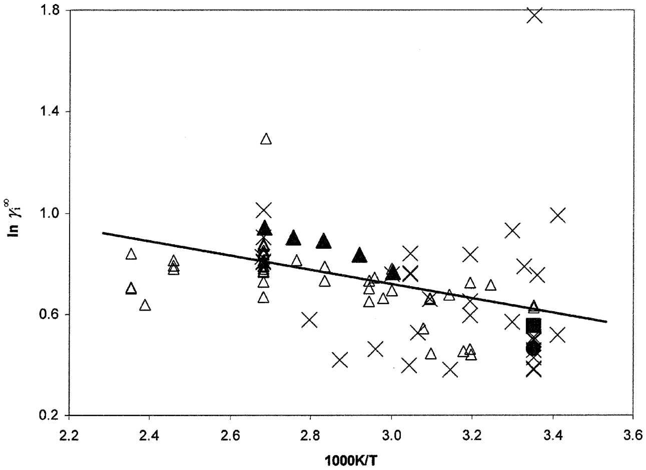

Figure 1. Literature values of the activity coefficients at infinite dilution of methanol as function of the reciprocal temperature: ×, Kojima et al.[6] and Dechema;[7] △, from vapor−liquid equilibria;[8] ▲, Christensen;[9] ●, Giralt et al.;[10] ■, Hwang et al.[11]

temperature of the oven was kept constant by means of a cooling coil, which was connected to a thermostatic bath filled with water at 5 °C. In this way, the temperature of the oven was stable to within ±0.02 K and could be measured within an accuracy of ±0.01 K. A flame ionization detector at 250 °C was used for the determination of the components in the carrier gas.

For a series of experiments, the column stays in the gas chromatograph, and the same sample was injected several times. In this way, the correction could be determined as function of the time of the experiment.

Results and Discussion

Initially, a reference component has to be chosen. In two databases,[6,7] 35 activity coefficients at infinite dilution are reported for methanol in water in the temperature range of (293 to 373) K. In Figure 1, the logarithms of the activity coefficients at infinite dilution as a function of the reciprocal temperature are plotted together with some data from VLE experiments.[8] From Figure 1, it can be concluded that there is a lot of scatter in the published data. From linear regression analysis of all of the data of the direct measured activity coefficients at infinite dilution,[6,7] an activity coefficient of 1.85 can be calculated for methanol in water at 295.15 K. From recommended data sets,[8] an activity coefficient at infinite dilution for methanol in water at 298.15 K of 1.83 could be calculated with the Wilson equation for the correlation of activity coefficients from VLE data. Ten directly measured activity coefficients at infinite dilution at 298.15 K are reported for methanol, which are close together. In the work reported here, we took the average of those data points at 298.15 K as a reference value for methanol by rejecting the outlyer of 5.92, so the reference value used was $\gamma^{\infty}_{\text{methanol}} = 1.60$ with a standard deviation of 0.06. This can result in an additional systematic error of a maximum of 3 % in the reported values of the activity coefficients at infinite dilution.

For the calculation of activity coefficients from the experimental work, the vapor pressures of the pure components are obtained from the literature, and the values at 298.15 K are given in Table 2. For the calculation of the activity coefficients at infinite dilution from the Henry's law constants, the vapor pressure as a function of the temperature was used as given in the mentioned literature. The vapor pressure of *cis*-4-heptenal is extrapolated from an estimated normal boiling point[13] of 412.3 K and a supplier-given vapor pressure of 60 °C at 25 mmHg. The vapor pressure data of acetoin is given in the Landolt−Bornstein data[16] and is not in good agreement with vapor pressure data given in Beilstein (E III,1, page 3206 and E IV.1, page 3991). The vapor pressures of *cis*-4-heptenal and acetoin are used only for the calculation of the gas-phase nonidealities.

Table 2. Some Properties of the Components at a Temperature of 298.15 K[a]

component	B/cm^3·mol^{-1}	B_{23}/cm^3·mol^{-1} (T)	V/cm^3·mol^{-1}	$P°$/Pa
methanol	−1693 (lb)	35.57	40.70 (Y)	16 941 (P)
ethanol	−2857 (lb)	47.75	58.51 (Y)	7876.4 (P)
propanol	−3132 (lb)	53.98	74.94 (Y)	2785.5 (P)
acetone	−2012 (lb)	50.25	73.93 (Y)	30 803 (P)
2-butanone	−2571 (lb)	55.91	90.21 (Y)	12 034 (P)
2-pentanone	−3558 (T)	61.62	107.40 (Y)	4717.4 (P)
2-hexanone	−5232 (T)	69.14	124.12 (Y)	1541.1 (P)
diacetyl	−2159 (T)	56.09	87.40 (s)	7453.9 (St)
methyl sulfide	−914 (lb)	44.64	73.09 (Y)	64 503 (P)
cis-4-heptenal	−6141 (T)	73.62	132.43 (s)	413.46 (*)
acetoin	−5163 (T)	61.52	86.98 (s)	1087.9 (*)
acetaldehyde	−1210 (lb)	43.89	56.94 (Y)	119 802 (Y)

[a] (lb) Recommended values given in the Landolt−Bornstein data;[12] (T) calculated using Tsonopolous' method for polar liquids;[13] (Y) data handbook by Yaws;[14] (s) data from the chemical supplier; (P) from section D in Appendix A of Poling et al.;[13] (St) from Stephenson and Malanowski;[15] (*) see text.

Table 3. Effect of the Correction on the Result of the Determination of the Activity Coefficient at Infinite Dilution of Diacetyl in Water with Methanol as a Reference Compound at 298.15 K[a]

injection	retention time/min		activity coefficient at infinite dilution	
time/min	diacetyl	methanol	uncorrected	corrected
0.00	55.62	195.78	12.57	13.36
281.68	49.24	172.80	12.54	13.36
472.55	44.32	159.00	12.82	13.55
663.37	40.69	143.10	12.57	13.33
854.13	36.29	127.63	12.58	13.36
1044.93	31.90	111.75	12.53	13.40
1235.68	27.95	97.26	12.45	13.23
1349.03	25.57	88.52	12.39	13.11
	average:		12.56	13.34
	absolute standard deviation:		0.12	0.13
	relative standard deviation/%:		0.99	0.94

[a] Retention time of the unretained compound = 0.16 min.

For the corrections of the gas-phase nonidealities, we also need the second virial coefficients and liquid molar volumes of the pure components and the cross virial coefficients. Literature data and estimated values of these properties at 298.15 K are given in Table 2. The calculated correction factor (exp Φ_A of eq 8) for the nonideality of the gas phase is then between 1.01 and 1.03. In this work, a relative method is used, so the total influence of this correction is very low according to eq 4.

In Table 3, the effect is reported for the correction of the solvent loss on the activity coefficient at infinite dilution of diacetyl with methanol as the reference component. From the results of Table 3, it can be concluded that the corrected value of the activity coefficient at infinite dilution is 6.2 % higher than the uncorrected value. In the literature, we found three values of the activity coefficient at infinite dilution of diacetyl in water at 298.15 K: 3.95,[17] 13.2,[18] and 10.2.[19] Table 3 also shows that experiments with different stationary-phase loadings as a result of stripping

Table 4. Henry's Law Coefficients and Activity Coefficients at Infinite Dilution in Water

reference component	T/K	H_i/kPa measured[a]	H_i/kPa corrected	γ_i^∞	n	$\sigma(\gamma_i^\infty)$ or $\sigma(H_i)$[b]
Ethanol						
methanol	298.15	29.8	29.7	3.77	9	0.048
Propanol						
methanol	298.01	37.5	37.2	13.4	12	0.26
	298.03	37.4	37.1	13.3	17	0.15
	298.10	37.6	37.3	13.4	19	0.23
	298.04	37.4	37.1	13.3	14	0.16
	298.10	37.5	37.2	13.3	9	0.24
Acetone						
methanol	298.01	230	233	7.62	13	0.13
propanol	298.03	231	234	7.64	16	0.071
	298.04	232	236	7.68	14	0.052
	298.03	231	236	7.70	19	0.035
	298.17	232	237	7.70	24	0.058
	298.01	230	235	7.68	13	0.080
	298.04	232	237	7.74	14	0.040
2-Butanone						
methanol	297.85	322	322	25.8	26	0.20
propanol	298.15	327	330	26.1	12	1.00
2-Pentanone						
propanol	298.15	695	696	148	3	1.3
	297.85	595	597	129	13	2.6
2-Hexanone						
propanol	297.85	539	538	319	23	2.6
	298.15	455	454	265	12	9.7
Diacetyl						
methanol	298.10	100.9	100.4	13.3	8	0.15
propanol	298.10	100.7	101	13.3	27	0.12
	298.10	98.2	98.5	13.2	25	0.19
	298.17	98.1	98.3	13.2	33	0.08
	298.17	97.6	97.9	13.1	36	0.06
	298.17	97.8	98.1	13.2	29	0.11
Methyl Sulfide						
methanol	298.01	11114	11 260	175	10	4.3
propanol	298.03	10771	10 912	170	16	7.8
acetone	298.03	10907	11 140	173	17	6.2
	298.01	10863	11 096	173	13	6.0
	298.01	10961	10 952	171	14	6.4
	298.07	11484	11 475	178	32	4.0
	298.02	11819	11 810	184	9	1.9
	298.02	11878	11 868	185	32	2.6
cis-4-Heptenal						
acetone	298.07	642	625.4		21	7.1
	298.07	641	624.4		24	6.3
	298.07	657	640.3		23	11.4
Acetoin						
acetone	298.09	99.9	97.6		23	0.9
	298.09	101.6	99.3		18	1.4
	298.12	100.4	98.1		33	1.4
	298.10	98.2	96.0		18	4.5
	298.11	99.1	96.8		21	1.5
Acetaldehyde						
acetone	298.13	471	488	4.08	20	0.02
	298.13	475	492	4.11	22	0.02
	298.15	479	496	4.14	21	0.03
	298.13	477	495	4.13	17	0.01
	298.13	483	501	4.18	22	0.02

[a] Correction factor E included, but without the correction of the gas-phase nonideality; n = number of measurements within an experiment. [b] The standard deviation is defined as $\sigma = \sqrt{\{(\sum x_i^2 - (\sum x_i)^2)/n\}/(n-1)}$ with x_i being the individual measured activity coefficient at infinite dilution or the Henry's law coefficient.

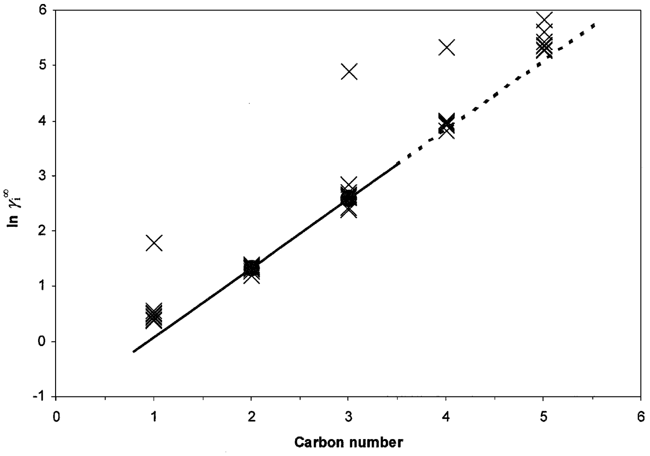

Figure 2. Natural logarithm of the activity coefficients at infinite dilution of alkanols as a function of the carbon number of the alkanol: ×, Kojima et al.[6] and Dechema;[7] ●, this work; the line and the dotted line are the linear regression of the measured values of this work.

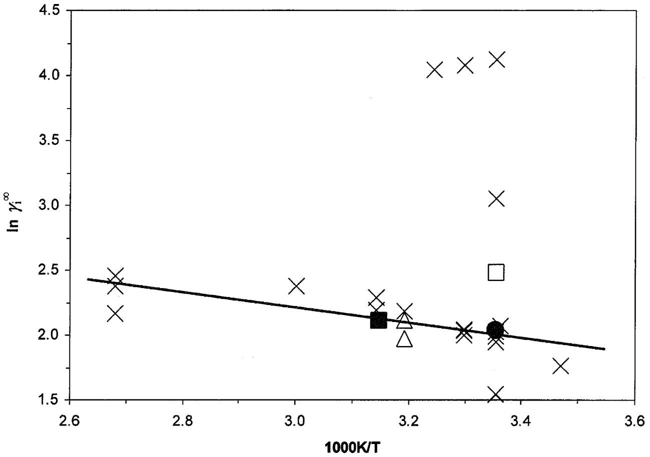

Figure 3. Natural logarithm of the activity coefficients at infinite dilution of acetone as a function of the reciprocal temperature: ×, Kojima et al.[6] and Dechema;[7] ■, Hartwick and Howat;[20] △, Shaw and Anderson;[21] □, Yaws;[14] ●, this work.

the water from the column resulted in similar values for the activity coefficient at infinite dilution. This shows that partitioning is the only retention mechanism in the experiments. Also in the experiments with the other solutes we used column loadings between 0.5 and 0.2 g of water in the column.

In Table 4, the results of the other experiments are given. In Figure 2, the measured results of ethanol and propanol are compared with literature data at 298.15 K for alkanols with a carbon number of 1 up to 5. The average of the 14 data points for ethanol at 298.15 K is 3.77 (standard deviation of 0.19). This is in good agreement with the reported activity coefficient at infinite dilution of ethanol in Table 4. The average of the 10 data points for propanol at 298.25 K is, after rejecting the value of 133.5, 13.70 with a standard deviation of 1.78. This is 0.35 higher than the reported activity coefficient in Table 4. We also used the measured average value of the activity coefficients at infinite dilution for propanol in water as a reference value ($\gamma_{\text{propanol}}^\infty = 13.35$).

In Figure 3, the measured results of acetone are compared with literature data. Only four values are comparable with our average result ($\gamma_{\text{acetone}}^\infty = 7.68$). Our work is in good agreement with the other data at different temperatures, especially with the data point of Hartwick and Howat[20] ($\gamma_{\text{acetone}}^\infty = 8.3$ at 317.15 K). Hartwick and Howat[20] reported a detailed experimental method with a modified static cell device for measuring activity coefficients at infinite dilution of volatile compounds in water. The

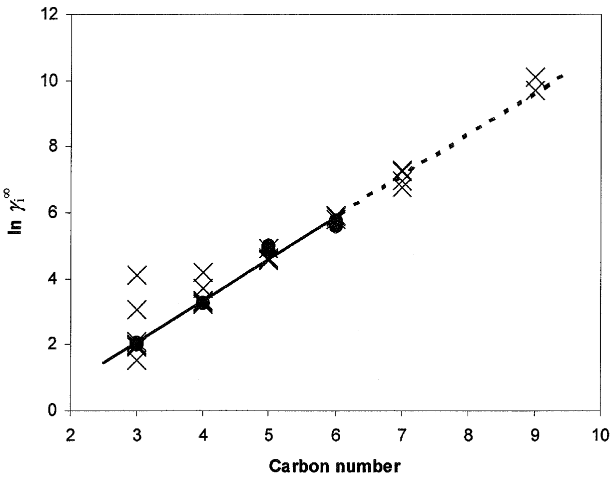

Figure 4. Natural logarithm of the activity coefficients of the methyl ketones as a function of the carbon number: ×, Kojima et al.[6] and Dechema;[7] ●, this work; the line and the dotted line are the linear regression of the measured values of this work.

average value of acetone was also used as a reference component in this work. From Table 4, it could be concluded that the choice of the reference component is not crucial to the results. For each component, a reference component is chosen with a retention time as close as possible to the retention time of the component. The retention time of acetone is nearly 5 times lower than the retention time of propanol and more than 6 times lower than that of methanol.

In Figure 4, the logarithm of the activity coefficients at infinite dilution of the methyl ketones (acetone, 2-butanone, 2-pentanone, and 2-hexanone) and literature data with carbon numbers of $n = 3$, 4, 5, 6, 7, and 9 are plotted against the carbon number of the ketones. This results in nearly linear behavior, and the linear extrapolation of the reported data of this work agrees with the literature data at higher carbon numbers.

The activity coefficient at infinite dilution of diacetyl ($\gamma^\infty_{\text{diacetyl}}(\text{average}) = 13.21$) is comparable with the reported value of Snider and Dawson[18] ($\gamma^\infty_{\text{diacetyl}} = 13.2$). The standard deviations of the results for methyl sulfide (Table 4) are relatively high because of the small net retention time (50 times smaller than with acetone). The average value of the activity coefficient at infinite dilution of methyl sulfide ($\gamma^\infty_{\text{methylsulfide}}(\text{average}) = 176.2$) is comparable to the mentioned value of 174 by Kojima et al.,[6] which was calculated from mutual solubility data. Sander[22] published a database of Henry's law constants for compounds in water. The calculated activity coefficients at infinite dilution of methyl sulfide from this database are given in Table 5. Most values are comparable with the results of this work.

For the component *cis*-4-heptenal, we could not find literature data on Henry's law constants or activity coefficients. For the component acetoin, activity coefficients at infinite dilution are found from extrapolated vapor−liquid equilibrium data at 750 mmHg:[8] 5.01, 5.57, and 4.78. The first two values were obtained from VLE at almost infinite dilution.

Kojima at al.[6] and Dechema[7] mentioned a few activity coefficients at infinite dilution of acetaldehyde (Table 6), and from Sander's[22] database activity coefficients at infinite dilution could also be calculated (Table 5). From extrapolated vapor−liquid equilibrium data from the literature,[8] an activity coefficient at infinite dilution for acetaldehyde at 298.15 K of 4.2 ± 0.5 could be fitted. The activity coefficient at infinite dilution, measured with the LLC method (Table 6), seems to be too high in comparison with the other literature data, so the average activity coefficient at infinite dilution of acetaldehyde in this work ($\gamma^\infty_{\text{acetaldehyde}}(\text{average}) = 4.13$) is comparable with literature data.

Table 5. Henry's Law Constants (k^θ_{H}) Given by Sander[22] at 298.15 K and the Calculated Activity Coefficients at Infinite Dilution

H/kPa	γ_i^∞	H/kPa	γ_i^∞	H/kPa	γ_i^∞
		Methyl Sulfide			
10 200	158	10 000	155	11 700	181
35 000	543	12 700	198	70 100	1087
9000	140	9000	140	11 700	181
7900	122	10 000	155		
		Acetaldehyde			
374	3.12	330	2.75	330	2.75
374	3.12	431	3.60	3300	27.5
431	3.60	374	3.12	401	3.34
510	4.26	566	4.73		

Table 6. Activity Coefficients at Infinite Dilution of the Component Acetaldehyde from the Databases of Kojima et al.[6] and Dechema[7]

T/K	γ_i^∞	method[a]	T/K	γ_i^∞	method[a]
293.15	3.59	GC	303.15	26.04	LLC
297.45	4.36	GC	303.15	4.43	HS
298.15	3.94	GCR	308.15	32.45	LLC
298.15	29.4	LLC	313.15	3.71	GC
303.15	4.36	GC			

[a] Method: GCR and GC − a gas−liquid chromatographic method with and without gas-phase correction, respectively; LLC − a liquid−liquid chromatographic method; HS − a headspace chromatographic method.

Conclusions

The relative stationary gas−liquid chromatographic method for the determination of activity coefficients at infinite dilution is a reliable method for the solvent water.

A correction for the solvent loss during a series of measurements is necessary. This correction is often larger than the correction of the gas-phase nonideality.

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