Refined non-steady-state gas–liquid chromatography for accurate determination of limiting activity coefficients of volatile organic compounds in water
Application to C$_1$–C$_5$ alkanols

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Abstract

This work presents a new refined method of non-steady-state gas–liquid chromatography (NSGLC) suitable for determination of limiting activity coefficients of VOCs in water. The modifications done to the original NSGLC theory address its elements (as the solvent elution rate from the column) as well as other new aspects. The experimental procedure is modified accordingly, taking advantage of current technical innovations. The refined method is used systematically to determine limiting activity coefficients (Henry's law constants, limiting relative volatilities) of isomeric C$_1$–C$_5$ alkanols in water at 328.15 K. Applied to retention data measured in this work the refined NSGLC theory gives values 15–20% higher than those from the original approach. The values obtained by the refined NSGLC method agree very well (typically within 3%) with the most reliable literature data determined by other experimental techniques, this result verifying thus the correct performance of the refined method and demonstrating an improved accuracy of the new results.
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1. Introduction

Limiting activity coefficient (γ^∞) is a fundamental thermodynamic quantity characterizing the behavior of an organic solute in highly dilute solutions and governing its phase distribution in such systems. Reliable data on this quantity are required for numerous practical and theoretical applications in a variety of chemical disciplines ranging from process engineering, through environmental chemistry and theory of solutions, to biochemistry. Today, a number of experimental methods is available to measure the limiting activity coefficients. Yet, further development in this direction is needed to improve the measurement accuracy and extend the method applicability.

One of the traditional routes for the experimental determination of the limiting activity coefficients is the GLC retention measurement. In its classical version, the GLC method can be applied well only to volatile solutes in effectively non-volatile solvents; a volatile stationary phase is continuously stripped from the column by the carrier gas flow, which causes a continuous change of the retention of injected solute samples. To achieve the desired extension of the classical GLC technique to volatile solvents (e.g. water), one has three different possibilities: (i) to presaturate the carrier gas by the solvent vapor [1,2], (ii) to measure the retention relatively to a reference solute which is injected simultaneously with the studied solute in a mixed sample [3,4], (iii) to measure the retention as a function of the sample injection time [5,6]. The first procedure solves the problem of the volatile stationary phase only partially: though the elution of the volatile stationary phase decelerates, it does not completely cease due to the pressure drop across the column, and the knowledge of the exact amount of the solvent in the column continues to be required for the calculation of γ^∞. A distinct merit of the second procedure is that the knowledge of the stationary phase amount is not at all needed, but the determination is relative, fully relying on the knowledge of the value γ^∞ for a reference solute. The third procedure, proposed and applied by Belfer and coworkers

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[5–8] and denoted as non-steady-state gas–liquid chromatography (NSGLC) requires neither of these entries. However, despite this strength and other advantages (simplicity, speed, robustness), the NSGLC technique appears to be considered less accurate than other methods and has been only rarely used. Moreover, preliminary measurements by Belfer's NSGLC method carried out formerly in our laboratory on aqueous oxygenates showed excessive scatter and a definite bias towards lower γ^∞ values.

Being motivated by the facts given above and focusing on water as a solvent, we have explored Belfer's method and found some potential for its improvement. As an outcome, we present in this paper a new refined NSGLC theory, together with the experimental procedure and retention data treatment modified accordingly. The refined method is then applied systematically to determine limiting activity coefficients of C_1–C_5 alkanols in water. Careful comparison of the results with the most reliable γ^∞ values obtained by other experimental methods allows us to verify the correct performance of the refined NSGLC method and to demonstrate an improved accuracy of the new results.

2. Theory

2.1. Classical GLC

In the classical GLC working with an effectively non-volatile stationary phase (solvent), the limiting activity coefficient of solute (1) can be calculated from the retention measurements using the following well-known formula [9]

$$\gamma_1^\infty = \frac{RTn_2}{p_1^s V_N} \tag{1}$$

Here, p_1^s stands for the solute vapor pressure at the column temperature T, n_2 for the molar amount of the solvent (2) in the column, and V_N for the solute net retention volume. Representing the difference of the corrected retention volume V_R^0 and the corrected mobile phase holdup of the column (column "dead" volume) V_M^0, the net retention volume is related through

$$V_N = (t_R - t_M)jF \tag{2}$$

to the measured solute retention time t_R, the retention time of a non-sorbed solute t_M, the carrier gas flow rate F at temperature T and pressure p_o at the column outlet, and the compressibility correction j for the column pressure drop

$$j = \frac{3}{2} \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1}, \tag{3}$$

p_i being the column inlet pressure. Eq. (1) assumes the ideal behavior of gas phase and the validity of Henry's law.

2.2. Original non-steady-state GLC

In the non-steady-state GLC, working with a volatile stationary phase (solvent), the amount of solvent in the column decreases as the solvent continuously evaporates into the carrier gas. As a consequence, the retention of gradually injected solute samples decreases as well. According to Eq. (1), the decrease in

the net retention volume is directly proportional to the decrease in the amount of solvent

$$dV_N = \frac{RT}{p_1^s \gamma_1^\infty} dn_2 \tag{4}$$

If the carrier gas flow rate F is kept constant and one assumes that neither the compressibility correction j, nor the column "dead" volume V_M vary with time, the differentiation of Eq. (2) gives

$$dV_N = jF \, dt_R \tag{5}$$

At constant jF and T, Belfer et al. [6] consider that the loss of solvent from the column due its evaporation is given by the following relation

$$dn_2 = -\frac{p_2^s jF}{RT} dt \tag{6}$$

Combining Eqs. (4)–(6), one gets

$$\gamma_1^\infty = -\frac{p_2^s/p_1^s}{dt_R/dt} \tag{7}$$

Thus, according to Belfer et al. the dependence of the retention time of a solute on the time of its injection into the column is linear and the limiting activity coefficient can be determined from the slope of this dependence using Eq. (7).

2.3. Refined non-steady-state GLC

The refined theory of NSGLC modifies Belfer's original approach in the following five aspects.

1. Assuming that the carrier gas is saturated with the solvent vapor at the column outlet, the solvent elution rate from the column is at a constant T determined solely by the outlet carrier gas flow rate and does not depend on the pressure gradient across the column. Thus, Eq. (6) employed by Belfer et al. is considered to be incorrect and is replaced by

$$dn_2 = -\frac{p_2^s F}{RT} dt \tag{8}$$

2. Since our monitoring of the pressure gradient across the column has shown that this gradient changes consistently and significantly with the amount of solvent water in the column (and hence with time), the compressibility correction is, contrary to the original Belfer's theory, no longer considered to be time-independent. As a result, Eq. (5) is replaced by

$$dV_N = F \, d(jt_R) = F \, dt_R^0 \tag{9}$$

where $t_R^0 = jt_R$ is the corrected retention time. By joining Eqs. (8) and (9) with Eq. (4), the relation for limiting activity coefficient is

$$\gamma_1^\infty = -\frac{p_2^s/p_1^s}{dt_R^0/dt} \tag{10}$$

Although Eqs. (10) and (7) look very similar, the replacement of the retention time by the corrected retention time, as inferred

here, has important consequences. Since $j < 1$, Eq. (7) leads to systematically lower values of γ_1^∞ than are those calculated by Eq. (10). Even for relatively small pressure gradients (30–40 kPa) corresponding to a short packed column as that used in this work, the difference attains a level of 15–20%. Note also that the application of Eq. (10) additionally requires the pressure drop to be monitored during the entire NSGLC experiment as well as the column outlet pressure (atmospheric pressure) to be determined.

The refined NSGLC approach comprises three more modifications of the original theory addressing a somewhat different picture of solvent elution from the column than that put forward by Belfer et al. [6]. These authors considered that the solvent coats the solid support uniformly as a film which keeps approximately constant thickness during the elution, being depleted only from the inlet side of the column. However, visual observations in our preliminary experiments with glass columns showed that water introduced as a solvent through a hot injection port condensed on a silanized solid support in the form of small droplets, more water being deposited at the column inlet than further downstream. Neither the depletion of solvent from the column is limited to the column-inlet front, but due to the existing pressure drop this depletion partly occurs throughout the column. As a result, our conception for further considerations is that some water continues to be present in all parts of the column over its lifetime. In spite of being unavoidably crude, the adopted conception is believed to be better suited for the water solvent than the original picture. Anyway, the following modifications affect the calculated value of γ_1^∞ to only a lesser extent, the effects partially compensating each other.

3. Contrary to the classical GLC (non-volatile stationary phase), the mobile phase in NSGLC is not the neat carrier gas, but the carrier saturated with the solvent vapor. Following the procedure described in the monograph of Conder and Young [9], one can derive that in this situation the compressibility correction j is given by the same type of relation as Eq. (3), but with the column inlet and outlet pressures replaced by the respective carrier gas partial pressures. Hence, in the refined NSGLC approach we consider the compressibility correction in the form

$$j = \frac{3}{2} \frac{[(p_i - p_2^s)/(p_o - p_2^s)]^2 - 1}{[(p_i - p_2^s)/(p_o - p_2^s)]^3 - 1} \tag{11}$$

For experimental conditions used in this work (see below), the effect of this modification on the calculated value of γ_1^∞ is about +3%.

4. During the period of time the solute takes to pass through the column, the amount of solvent in the column changes. Thus, the observed $t_{R,exp}^0$ is not the "point" value corresponding to the instant of the sample injection t_{inj}, but rather the mean value $\overline{t_R^0}$ over the interval from the instant of the sample injection to the instant of its detection at the column outlet

$$t_{R,exp}^0 = \overline{t_R^0} = \frac{1}{t_R} \int_{t_{inj}}^{t_{inj}+t_R} t_R^0 \, \mathrm{d}t \tag{12}$$

Taking into account that the dependence $t_R^0 = f(t)$ is linear (see Eq. (10)), one can however readily show that $\overline{t_R^0}$ corresponds to the "point" value at the midpoint of the respective time interval $\langle t_{inj}, t_{inj} + t_R \rangle$, and hence

$$t_{R,exp}^0 = \overline{t_R^0} = t_R^0(t = t_{inj} + t_R/2) \tag{13}$$

In the refined NSGLC approach, the experimentally determined t_R^0 is not therefore ascribed to $t = t_{inj}$, but to $t = t_{inj} + t_R/2$. For systems studied in this work, this modification translates into a slight (2–5%) decrease of the calculated value of γ_1^∞.

5. When deriving Eq. (10), we have assumed like Belfer et al. did, that the column holdup volume is constant. This is exactly so in the classical GLC where the stationary phase is nonvolatile. However, in the NSGLC, where the solvent is eluted from the column, the column holdup volume increases in the same manner as the solvent volume in the column V_L decreases

$$\mathrm{d}V_M^0 = -\mathrm{d}V_L \tag{14}$$

Relating $\mathrm{d}V_L$ to $\mathrm{d}n_2$ and expressing the latter by Eq. (8) gives

$$\mathrm{d}V_M^0 = F \frac{p_2^s v_2^L}{RT} \, \mathrm{d}t \tag{15}$$

where v_2^L is the solvent molar volume at the column temperature. Then, the following equation for the change of the net retention volume will hold instead of Eq. (9)

$$\mathrm{d}V_N = \mathrm{d}V_R^0 - \mathrm{d}V_M^0 = F\left(\mathrm{d}t_R^0 - \frac{p_2^s v_2^L}{RT} \, \mathrm{d}t\right) \tag{16}$$

On combining Eqs. (16) and (8) with Eq. (4), one gets

$$\gamma_1^\infty = -\frac{p_2^s/p_1^s}{(\mathrm{d}t_R^0/\mathrm{d}t) - (p_2^s v_2^L/RT)}, \tag{17}$$

a refinement of Eq. (10) which takes into account the column holdup volume variation. As explicitly seen when Eqs. (17) and (10) are compared

$$\gamma_1^\infty(\text{Eq. (17)}) = \frac{\gamma_1^\infty(\text{Eq. (10)})}{1 + K_{gl}}, \tag{18}$$

the effect of holdup volume variation on the calculated value of γ_1^∞ is fully determined by $K_{gl} = \gamma_1^\infty p_1^s v_2^L/RT$, the solute gas–liquid partition coefficient.

For systems studied in this work ($K_{gl} < 0.01$), this effect is negligible (within 1%), but at a higher temperature or for solutes of a greater volatility may become appreciable.

2.4. Applicability of the non-steady-state GLC

In general, the applicability of the NSGLC method is constrained by system volatility conditions. The basic requirement is that the volatility of the solute from the dilute solution exceeds the volatility of the solvent, otherwise the solvent elutes before the solute. Combining Eqs. (1) and (2) with the integrated form

of Eq. (8) yields the link between the retention time t_R and the remaining column lifetime t_{life}

$$t_R = \frac{t_{life} p_2^s}{j p_1^s \gamma_1^\infty} + t_M, \tag{19}$$

which on imposing the condition $t_R < t_{life}$ and considering $t_M \ll t_{life}$ gives the following lower bound for the solute limiting relative volatility α_{12}^∞

$$\alpha_{12}^\infty = \frac{\gamma_1^\infty p_1^s}{p_2^s} > \frac{1}{j} \tag{20}$$

Note that it is only for column pressure gradients approaching zero, when the permissible value of α_{12}^∞ can theoretically approach unity. The upper bound of α_{12}^∞ follows from the fact that as α_{12}^∞ increases, the measured derivative dt_R^0/dt approaches zero and its determination is greatly affected by experimental errors. Concrete value of the upper bound depends on the measurement precision and the error tolerance; a practical upper bound may be around $\alpha_{12}^\infty = 100$. Respect to the volatility of the solvent, there are constraints, too. High solvent vapor pressures lead to prohibitively short column lifetimes, while low p_2^s values cause the solvent elution from the column (i.e. the driving mechanism of NSGLC) to be too slow. In both cases, problems of precision arise. As a result, the applicability of NSGLC for water solvent is expected to be in the range from the room temperature to about 350 K.

3. Experimental

3.1. Materials

Alkanols used as solutes were analar grade commercial chemicals. With the exception of 2-methylpropan-2-ol, the substances were used as purchased. The commercial sample of 2-methylpropan-2-ol, which exhibited a markedly lower melting temperature (291 K) than that tabulated (298.8 K [10]), was recrystalized using a Vigreaux column to meet the tabulated melting temperature value. In any case, purity of solutes is not critical, since impurities which would affect the determination of the retention are separated by the chromatographic process itself. Water used as the solvent was distilled and subsequently treated by Milli-Q Water Purification System (Millipore, USA).

3.2. Apparatus and procedure

The gas chromatograph employed was Agilent 6890 Plus (Agilent Technologies, USA) with a flame ionization detection (FID) and a 0.5 m long stainless steel column of 1/8 in. o.d. packed with a bare solid support Inerton Super 0.125–0.160 mm (Lachema, Czech Republic). The coating of the support with the solvent water was realized in situ by manually injecting the water with a gas-tight syringe (Hamilton, Switzerland) into the column through the respective hot injection port (150 °C). Here, water is flash-evaporated and vapors swept into the column (maintained at the experimental temperature 55 °C) condense on the solid support forming thus the coating. The oven temperature

setting was checked through an independent measurement by a calibrated platinum resistance thermometer. Solutes were injected automatically, in the form of their dilute aqueous solutions (solute mole fraction approximately 0.001), by means of a 7683 Series Agilent AutoInjector. The injected sample volumes were 0.1 µL. Nitrogen at a flow rate of 8 mL/min was used as a carrier gas. The detector was operated at 150 °C and at the following flow rates of gases: hydrogen 30 mL/min, air 350 mL/min, and make-up nitrogen 15 mL/min. The operation of the GC, including the controls of all gas flow rates and zone temperatures, sample injection, data acquisition (FID signal and column inlet gauge pressure) and processing, was provided by an interfaced personal computer using Agilent ChemStation software.

The experimental procedure begins with injecting 400 µL of water to load the column with the solvent. As a consequence of the flash-evaporation of water in the hot injection port the column inlet gauge pressure abruptly increases from the initial value of about 28 kPa to about 60 kPa. Shortly after the injection of the solvent water, there is some displacement of water droplets from the column grossly disturbing the FID signal and usually extinguishing the flame. Nevertheless, equilibration is quite rapid, so the flame can be re-ignited in 10–15 min and a well-stable low-level base line is recovered within next 15–20 min. By that time the inlet column gauge pressure amounts typically to 37–40 kPa. As soon as this stage has been reached, a sample injection sequence is started. In order to accumulate as many retention data points as possible during the column lifetime, a new injection of the sample follows immediately after the previous sample has been eluted. The observed retention times of repetitively injected samples continuously decrease and so does the column inlet gauge pressure. Under the given experimental conditions, the elution of solvent water from the column is complete in about 3.5 h from the water loading injection. This situation is clearly indicated by a small, but abrupt drop of the base line. Since then, the inlet column gauge pressure, which has dropped back to its "bare column" value, does not change any more and any subsequent sample injections result in the same time-independent retention time.

4. Results and discussion

4.1. Data processing

The NSGLC retention experiments were carried out at 328.15 K for a set of 15 C_1–C_5 alkanols comprising all possible isomers with the exception of 2,2-dimethylpropan-1-ol. This pentanol isomer was not considered because of proximity of its melting temperature (327 K) to the experimental temperature and a great uncertainty in available vapor pressure data. Measured retention data were processed according to the refined NSGLC approach described in this work. The retention times were translated to the corrected values t_R^0, the corresponding compressibility correction being calculated for each sample injection from Eq. (11) at the half-time of the sample retention. Following Eq. (13) the corrected retention times were assigned to the respective times $t = t_{inj} + t_R/2$ and

Table 1
Pure solute vapor pressures, limiting activity coefficients, limiting relative volatilities, and Henry's law constants for C_1–C_5 alkanols in water at 328.15 K along with respective uncertainties[a]

Solute	p_1^s (kPa)	Reference	$s_{rel}(p_1^s)$ (%)	γ_1^∞	$s(\gamma_1^\infty)$	α_{12}^∞	$s(\alpha_{12}^\infty)$	H_{12} (kPa)	$s(H_{12})$ (kPa)
Methanol	68.83	[14]	0.1	2.06	0.02	9.0	0.1	142	1
Ethanol	37.36	[14]	0.1	5.42	0.06	12.9	0.1	203	2
Propan-1-ol	15.77	[14]	0.1	18.9	0.1	18.9	0.1	297	2
Propan-2-ol	30.30	[14]	0.1	11.2	0.1	21.5	0.2	339	3
Butan-1-ol	6.06	[14]	0.2	61.6	0.7	23.7	0.2	373	4
Butan-2-ol	14.04	[14]	0.1	36.7	0.4	32.8	0.3	515	5
2-Methylpropan-1-ol	9.45	[15]	0.1	56.7	0.3	34.0	0.2	536	3
2-Methylpropan-2-ol	30.35	[14]	0.1	20.7	0.2	39.9	0.3	628	5
Pentan-1-ol	2.33	[14]	1	214	5	31.7	0.6	499	10
Pentan-2-ol	5.80	[14]	0.5	124	1	45.9	0.3	721	5
Pentan-3-ol	7.03	[11]	1	117	1	52.5	0.4	826	6
2-Methylbutan-1-ol	3.56	[16]	3	201	6	45.3	0.2	714	4
2-Methylbutan-2-ol	13.17	[16]	3	66.1	2.1	55.3	0.7	871	12
3-Methylbutan-1-ol	3.18	[11]	2	193	5	38.9	0.5	612	7
3-Methylbutan-2-ol	8.94	[11]	0.5	98.1	0.8	55.7	0.4	876	5

[a] Expressed by (relative) standard deviations and calculated as follows: $s(\alpha_{12}^\infty) \cong \alpha_{12}^\infty s_{rel}(dt_R^0/dt)$; $s(H_{12}) \cong H_{12} s_{rel}(dt_R^0/dt)$; $s(\gamma_1^\infty) \cong \gamma_1^\infty [s_{rel}^2(dt_R^0/dt) + s_{rel}^2(p_1^s)]^{1/2}$.

this set of data was subjected to linear regression. For all solutes studied, the data showed good linearity and little scatter as indicated by common statistical characteristics: the coefficient of determination (R^2) was typically higher than 0.999 and the standard deviation of fit lower than 2 s. The slopes thus obtained were of good precision ($s_{rel}(dt_R^0/dt) \cong 1\%$) and were used to calculate the limiting activity coefficients from Eq. (17). Carefully selected values of pure component vapor pressures from literature sources were employed in this calculation. For three pentanol isomers (pentan-3-ol, 3-methylbutan-1-ol, and 3-methylbutan-2-ol), where the information published did not permit reliable determination of p_1^s at 328.15 K, the simultaneous treatment of literature and some newly measured vapor pressure values together with thermal data greatly improved the situation [11].

Limiting activity coefficients determined according to the refined NSGLC theory and values of vapor pressures used in their calculation are listed in Table 1 along with their uncertainties expressed by respective standard deviations. The uncertainty in γ_1^∞ takes into account the uncertainty in both dt_R^0/dt and p_1^s (water vapor pressure is considered to be accurate) using the error propagation law. Given in Table 1 are also limiting relative volatilities

$$\alpha_{12}^\infty = \frac{\gamma_1^\infty p_1^s}{p_2^s} = -\frac{1}{(dt_R^0/dt) - (p_2^s v_2^L/RT)} \qquad (21)$$

and Henry's law constants

$$H_{12} = \gamma_1^\infty p_1^s = -\frac{p_2^s}{(dt_R^0/dt) - (p_2^s v_2^L/RT)} \qquad (22)$$

These two quantities are determined independently of p_1^s values and are thus burden only with the error of the NSGLC experiment proper.

In addition to the refined scheme, the measured retention data were processed also according to the original Belfer's theory to compare the performance of both approaches. The γ_1^∞ values from the original approach are by 15–20% consistently lower than those from the refined approach. At the same time the regression of retention data according to the original Belfer's theory is not as good as that of the refined approach; the standard deviation of fit being in all cases higher (by a factor ranging from 1.3 to 2.2) than for the refined scheme.

4.2. Method and results validation

In order to verify that the refined NSGLC theory performs correctly and to determine the accuracy of the results obtained, the limiting activity coefficients determined in this work were compared with the most reliable values currently available. Except for 3-methylbutan-2-ol, for which literature data are completely lacking, the comparison is presented for all solutes studied in Table 2. For each solute, however, the background and reliability of the "best" value used for the comparison may considerably vary. The reference γ_1^∞ values used for 1-alkanols, 2-methylpropan-1-ol, and 2-methylpropan-2-ol are of the highest reliability because they were calculated from the recommended $\gamma_1^\infty(T)$ dependences. Being established by comprehensive simultaneous correlations of γ_1^∞ data with calorimetric data on infinite dilution partial molar excess enthalpies $\bar{H}_1^{E,\infty}$ and heat capacities $\bar{C}_{P,1}^{E,\infty}$, in which goal-directed measurements carried out previously in our laboratory were combined with all those from literature, these recommended $\gamma_1^\infty(T)$ dependences are considered superior to any single γ_1^∞ values measured. For other alkanols studied recommended data have not been available and existing single γ_1^∞ values are at other temperature (typically 298.15 K) than that of interest (328.15 K). Nevertheless, for propan-2-ol, butan-2-ol, pentan-2-ol, pentan-3-ol, and 2-methylbutan-2-ol, where information on thermal quantities $\bar{H}_1^{E,\infty}$ (298.15 K) and $\bar{C}_{P,1}^{E,\infty}$ (298.15 K) is at disposal, these γ_1^∞ values can be brought from $T_0 = 298.15$ K to $T = 328.15$ K using

Table 2
Comparison of limiting activity coefficients determined by the refined NSGLC in this work with their most reliable values from literature obtained by other methods ($T = 328.15$ K)

Solute	$\ln \gamma_1^\infty$	
	This work	Literature
Methanol	0.72	0.73 [17]
Ethanol	1.69	1.66 [17]
Propan-1-ol	2.94	2.92 [17]
Propan-2-ol	2.42	2.39[a,b]
Butan-1-ol	4.12	4.15 [17]
Butan-2-ol	3.60	3.61[a,c]
2-Methylpropan-1-ol	4.04	4.07 [18]
2-Methylpropan-2-ol	3.03	3.04 [19]
Pentan-1-ol	5.36	5.40 [17]
Pentan-2-ol	4.82	4.82[a,d]
Pentan-3-ol	4.77	4.76[a,e]
2-Methylbutan-1-ol	5.30	5.30[g] [20]
2-Methylbutan-2-ol	4.19	4.07[a,f]
3-Methylbutan-1-ol	5.26	5.25[g] [21]

[a] Calculated from Eq. (23) using the following values of $\ln \gamma_1^\infty$, $\bar{H}_1^{E,\infty}$ (kJ mol^{-1}), and $\bar{C}_{P,1}^{E,\infty}$ (J K^{-1} mol^{-1}) at 298.15 K.
[b] 2.02 [22], -13.10 [23], 211.0 [24].
[c] 3.27 [25], -13.02 [26], 257.5 [24].
[d] 4.57 [25], -11.22 [27], 313.5 [24].
[e] 4.44 [28], -12.81 [28], 289.0 [29].
[f] 3.56 [21], -18.29 [26], 291.2 [30].
[g] The only value at 298.15 K.

the following relation

$$\ln \gamma_1^\infty(T) = \ln \gamma_1^\infty(T_0) + \frac{\bar{H}_1^{E,\infty}(T_0)}{RT_0}\left(1 - \frac{T_0}{T}\right)$$
$$+ \frac{\bar{C}_{P,1}^{E,\infty}(T_0)}{R}\left(1 - \frac{T_0}{T} + \ln\frac{T_0}{T}\right) \quad (23)$$

Since the thermodynamic extrapolation provided by Eq. (23) is sufficiently accurate, the reliability of the value recalculated to 328.15 K is given essentially by the reliability of the source value $\gamma_1^\infty(T_0)$. When choice was possible, source data of the highest credit were therefore selected. Because of the absence of thermal data for 2-methylbutan-1-ol and 3-methylbutan-1-ol, given for comparison in this case are the only literature values available at 298.15 K.

The comparison in Table 2 indicates that, with the exception of 2-methylbutan-2-ol, the γ_1^∞ values determined by the refined NSGLC method are in almost excellent agreement with the most reliable γ_1^∞ values currently available. The deviation corresponding to the probable combined uncertainty of the two values is typically within 0.04 in $\ln \gamma_1^\infty$, i.e. 4% in γ_1^∞. The highest deviation (0.12 in $\ln \gamma_1^\infty$) observed for 2-methylbutan-2-ol may be well due to the very old literature value, which is the only value available here for the comparison. In this context it should be noted that the excellent agreement observed for 2-methylbutan-1-ol and 3-methylbutan-1-ol is not very conclusive either, because the compared values are at different temperatures. Nevertheless, the similarity of the γ_1^∞ values at the two temperatures is plausible here, since for these pentanol isomers,

a maximum on $\gamma_1^\infty(T)$ is likely to occur within the respective temperature range.

In summary, the comparison in Table 2 provides a convincing proof of the correct performance of the refined NSGLC method and its improved accuracy. While the typical uncertainty of the presented γ_1^∞ values appears to be about 3%, the experimental error reported by Belfer et al. [6,7] for their original method was 10%. The measurement precision improved even to a greater extent: occasional replicates we carried out agreed to 2%, while the average relative deviation of replicated experiments obtained by Belfer et al. for a similar set of aqueous alkanols and ketones was 11.5% [7]. This striking amelioration of measurement precision could be achieved mainly thanks to technical refinements of the experimental procedure. Complete computer control of the present measurements allowed efficient long-term stabilization of experimental parameters. In this respect, the electronic mass-flow control is especially useful, as constancy of the carrier gas flow rate is a critically important prerequisite for precise and correct results to be obtained. The employment of FID instead of TCD is equally beneficial. FID compared to TCD offers for aqueous VOCs a low level baseline and a higher sensitivity, giving possibility to use much smaller sample sizes. True infinite dilution conditions can be thus effectively attained.

The effects of various experimental parameters were examined to rule out that the results obtained by the refined NSGLC procedure are fortuitous. Changing the carrier gas flow rate used and the sample size injected (solute concentration in the injected sample) within reasonable ranges we did not observe any significant effect on the resulting γ_1^∞. Variations in the amount of the solvent water loaded into the column did not present any effect either. As to small amounts of water introduced with sample injections, our calculations showed that they can be neglected and experiments carried out injecting neat solute vapor confirmed it.

A severe question concerns adsorption effects which always threaten to distort the interpretation of GLC retention data. In order to minimize the effect of solute adsorption occurring on the surface of the support, we used a highly inert support (Inerton Super) of low specific surface area (<1 m^2/g) which is very suitable for use with polar compounds. An indication that the adsorption on this solid support does not appreciably affect the retention in our chromatographic system follows from the fact that the retention times we measured on the dry column for methane (which was used as a holdup marker) and for the solutes studied differ only very slightly, the retention times for the latter being longer just by 1–2 s. In addition, we have performed also a few experiments using another support recommended for polar compounds, Chromosorb W-HP, which lead to identical results with those obtained on Inerton Super. Concerning the adsorption on gas/liquid interface, some estimates can be done on the basis of data measured recently by Roth et al. [31]. Thus, for ethanol solute, 100 μL of water in our column (about 30% loading w/w and the mid-stage of the column life) and assuming the surface area of water 1 m^2/g, it can be calculated that the relative contribution of the adsorption to the net retention would be 7.5%. It should be noted that this estimate however does not correspond directly to the effect on results of the performed
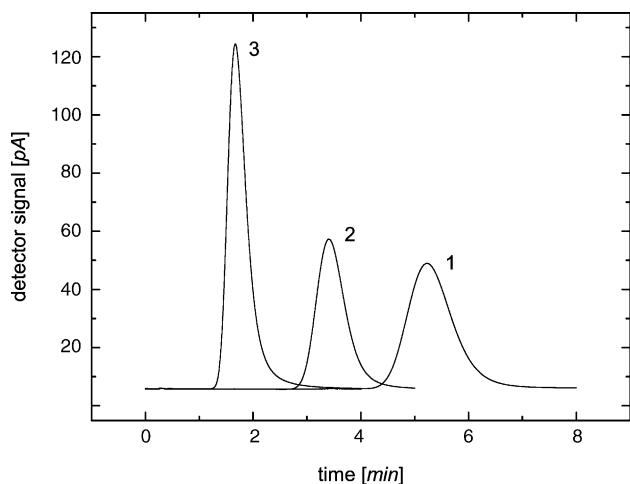
Fig. 1. FID signals in a typical NSGLC experiment: 2-methylpropan-2-ol in water at 328.15 K: (1) early stage; (2) mid-stage; (3) late stage of the column life.

NSGLC measurements which should be significantly smaller. The reasons are as follows: (1) The data of Roth et al. on which the above given estimate is based were measured at 288.15 K; at a temperature of 328.15 K at which our NSGLC measurements were carried out (and in general, at superambient temperatures where NSGLC is practical) the contribution of the adsorption should be considerably reduced. (2) At early stages of the column life, percentage loadings are still higher than that assumed in the calculation. (Note that such high loadings were possible thanks to the in situ loading procedure we employed.) (3) The decisive parameter in NSGLC is not the absolute value of the net retention, but its change with the time of solute injection and hence it is reasonable to expect that some compensation of adsorption effects on this parameter occurs. (4) The test criterion for the absence of adsorption effects used in GLC [9], $d(V_N/V_L)/dV_L = 0$, where V_L is the volume of the solvent in the column, is well met for all systems studied here, the independence of V_N/V_L on V_L being implied by the very good linearity of t_R^0 versus t observed. Note however, that for the test to be conclusive for NSGLC, possible adsorptive surfaces must not change their sizes proportionally with V_L, which is difficult to verify. (5) Some further support for the opinion that adsorption effects were negligible comes from the observation that, except for pentan-1-ol, the solute peaks were reasonably symmetrical. A sample of detector signals from a typical NSGLC experiment is presented in Fig. 1. Appreciable peak asymmetry encountered for pentan-1-ol correlates with the fact that its value of γ_1^∞ measured by NSGLC is 4% lower than the most reliable reference value, which also represents the largest proven deviation among all systems studied in this work. It appears that the result for pentan-1-ol starts to indicate possible problems with interfering adsorption effects which with still more hydrophobic and highly boiling solutes would become probably unavoidable, marking thus the applicability limitations of the present procedure.

The equations used in processing NSGLC retention data assume the gas phase is ideal. To assess the impact of this approximation on resulting γ_1^∞ values, the vapor-phase nonideality correction was calculated for three sample solutes, namely methanol, propan-1-ol, and pentan-1-ol. Since no theoretically adequate account of the vapor-phase nonideality has been presented in literature for the volatile liquid GLC, we employed the relation valid for a one-stage equilibrium system (Eq. (9) in ref. [12]) estimating the second virial coefficients from the Hayden–O'Connell correlation [13]. For methanol, propan-1-ol, and pentan-1-ol the calculated correction factors were, respectively, 1.029, 0.996, and 0.984. Consequently we believe that the effect of vapor-phase nonideality is within the estimated 3% uncertainty of our NSGLC γ_1^∞ values.

Last but not least, the internal consistency of the measured γ_1^∞ data was checked through a group contribution analysis. From the data for eight pairs of adjacent homologues (methanol excluded) the following average value of the CH_2 increment (at 328.15 K) with its standard deviation $\Delta_{CH_2}(\ln \gamma_1^\infty) = 1.214 \pm 0.012$ was obtained. This result can be considered as an additional proof of the quality of the present NSGLC measurements.

Acknowledgment

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