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Indirect headspace gas chromatographic method for vapor–liquid phase equilibrium study

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Abstract

This study reports on an indirect headspace gas chromatographic method for the study of vapor–liquid phase equilibrium (VLE). The method uses two sample vials filled with an identical solution of different volumes. The VLE partitioning coefficient of the solute is derived from the ratio of the peak areas of the solute from two independent headspace GC measurements of the two vials at equilibrium. Mathematical precision analysis and experimental verifications indicate that the volume ratio of the solutions in the two testing vials is a key parameter that dictates the accuracy of the method, and the present method can accurately measure a wide range of VLE partitioning coefficients of solutes. The method is rapid and automated. It does not require one to know the solute concentration in the system or to modify the sample matrix. Therefore, it has significant importance in many industrial, environmental and other practical applications. © 1998 Elsevier Science B.V.

Keywords: Headspace analysis; Vapor–liquid phase equilibrium; Partition coefficients; Thermodynamic parameters

1. Introduction

The study of the thermodynamic vapor–liquid phase equilibrium (VLE) of solutions has many practical applications, such as designing cost-effective industrial separation processes, estimating the emissions of volatile hazardous chemicals from wastewater streams into the atmosphere, and providing guidance in the selection of solvents for chemical reactors in which kinetic solvent effects are important. The measurements of the limiting activity coefficient of the solute under infinite dilution or the vapor–liquid partitioning Henry's constant can provide a better understanding of the mechanism of solute–solvent molecular interactions, for the development of theoretical thermodynamic models.

There are many techniques available for VLE studies. Comprehensive reviews on the measurement techniques and detailed comparisons of data obtained using these methods have been conducted [1–3]. The headspace gas chromatographic (HSGC) method gives a direct quantitative analysis of the vapor of a liquid sample matrix and, therefore, is very suitable for VLE studies. The traditional HSGC method [4–6] for VLE studies requires quantitative determination of the equilibrium solute concentration both in the vapor and in the liquid phases through direct measurements, using error-producing calibration procedures. Kolb et al. [7] developed another direct measurement technique, the vapor-phase calibration method, which simplifies the calibration procedure

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but requires that the solute concentration in the original sample is known. To obtain experimental simplicity and high accuracy for practical applications, automated indirect HSGC methods will be desirable. The methods of McAuliffe [8] and others [9,10] indirectly calculate the VLE partitioning from two separate headspace measurements. The first headspace analysis is conducted under equilibrium. The system equilibrium is then altered by mechanically venting part of the vapor. The second headspace analysis is conducted after the system reestablishes its equilibrium. With this type of indirect method, it is impossible to achieve measurement simplicity, automation and consistency, due to mechanical difficulties [7]. The multiple headspace extraction (MHE) method [11] was developed using the same concept. However, the method described in the literature [11] has many practical variants that could cause large experimental uncertainties.

The vapor–liquid partitioning coefficient is defined as the ratio of the equilibrium concentration of a solute in the liquid phase to that in the vapor phase in chromatography [12], i.e., $K=C_l/C_g$. Therefore, the inverse of K, H^*, is equal to the dimensionless Henry's constant, H_c, if the solute is under infinite dilution, i.e, $H^*=1/K=H_c$. Two independent measurements are required to obtain the K value of a VLE problem. Both liquid and vapor phases are directly analyzed in traditional methods, while two independent headspace measurements were made using the indirect headspace methods discussed above. From the physics of a VLE problem, a solute is transformed into two unknown phases from its initial state to the equilibrium state, and the solute mass is conserved during the transformation. In mathematical terms, the problem at phase equilibrium involves two unknown variables and can be solved with two equations. Therefore, it is sufficient and necessary to make two and only two independent measurements to solve a VLE problem using any indirect HSGC method.

Lincoff and Gossett [13,14] developed an indirect HSGC method to determine Henry's constants using equilibrium partitioning in closed systems (EPICS) and solute mass conservation. In their method, two sample vials were used, and the volume ratio of the two testing solutions was arbitrarily taken to be ten [13] and four [14]. The mass of the solute in the two solutions was equal [13], or the mass ratio was measured [14]. It was assumed that the solute in two solutions was under infinite dilution, therefore, the VLE partitioning coefficients of the solute in these two solutions are equal to the dimensionless Henry's constant at a given temperature. The advantages of the EPICS method are that no special apparatus is required and it can be easily automated. Henry's constant can be obtained by measuring the vapor concentration ratios from a pair of sealed vials with different solution volumes and solute concentrations through headspace gas chromatography (GC). However, the EPICS method has the following limitations: (1) It requires that one know the ratio of the amount of solute in the two solutions or the concentration; (2) because the concentrations of the solutions in the two testing vials were different, according to the experimental procedure proposed in the paper [14], the measurements were only valid when the method was based on the assumption that the solute was under infinite dilution, therefore, the procedure according to that described in their experiments is only applicable to measure the Henry's constant of the solute; and (3) furthermore, it requires standard addition to the original sample to obtain two testing solutions with different concentrations when applying the method to the analysis of an industrial or environmental sample of unknown concentration; consequently, one must know the solute mass or concentration of the original solution in order to obtain the mass ratio of the two testing solutions. Therefore, the experimental procedures proposed in the paper [14] are not applicable to solutions of unknown concentration and (4) the measurement error is very high when the Henry's constant is less than 0.1 (or $K>10$), as indicated by the precision analysis of Gossett [14].

Recently, Ettre et al. [12] developed another indirect headspace GC method, phase ratio variation (PRV), to measure the VLE partitioning coefficient K, based on solute mass conservation and equilibrium headspace (EHS). The authors derived a linear equation whose slope is related to K as a function of the vapor phase concentration, C_g, at equilibrium (measured by GC), solute concentration in the original solution C_l^o (constant), and a volume ratio parameter, β (known constant), which was called the phase (volume) ratio in the paper [12]. They then used four vials filled with the same solution but with different volumes. They conducted a headspace measurement for each vial at equilibrium to derive the slope of the linear equation, in order to determine the solute partitioning coefficient, K. The method requires at least four independent measurements to determine the slope or K. Again, the method is not accurate when large partitioning coefficients of K ($>$144) are to be measured, as indicated by Ettre et al. [12].

In this study, we derived an indirect HSGC method similar to the EPICS and PRV methods for rapid, automated and precise determination of the VLE partitioning coefficient of solute in any solution.

2. Methodology

We used two sample vials, both filled with the same sample solution but with different volumes, rather than two different solutions as in the EPICS method. We conducted a headspace analysis of each sample after phase equilibrium was established within each vial. The solute in the two systems had the same VLE partitioning coefficient, K, as the two systems were identical, which could be used to connect the two independent headspace measurements to determine the value of K. The following is the derivation of the present indirect HSGC method.

When a sample solution of volume V_l with a solute concentration of C_l^0 is introduced into a closed vial, the total number of moles, M, of the solute in the vial can be expressed as:

$$M = C_l^o V_l = C_l V_l + C_g V_g = C_g(V_l K) + C_g V_g = C_g[(V_l K) + V_g]\,, \tag{1}$$

where C_g and V_g are the concentration and volume of the solute in the vapor phase, respectively.

Therefore, the total number of moles of solute in two separate vials can be written as:

$$M_1 = C_l^o V_l^1 = C_g^1[(V_l^1 K) + V_g^1]\,, \tag{2}$$

$$M_2 = C_l^o V_l^2 = C_g^2[(V_l^2 K) + V_g^2]\,, \tag{3}$$

respectively.

The VLE partitioning coefficient, K, can be derived from Eqs. (2) and (3),

$$\frac{1}{K} = \frac{V_l^1(1 - C_g^1/C_g^2)}{C_g^1/C_g^2(V_t - V_l^1) - V_l^1/V_l^2(V_t - V_l^2)}\,. \tag{4}$$

The solute concentration in the vapor phase C_g is proportional to the peak area from the GC measurement. Thus, we have

$$C_g^1/C_g^2 = A_1/A_2. \tag{5}$$

Substituting Eq. (5) into Eq. (4), the VLE partitioning coefficient, K, or its inverse, H^*, can be determined

$$H^* = \frac{1}{K} = \frac{V_l^1(1 - A_1/A_2)}{A_1/A_2(V_t - V_l^1) - V_l^1/V_l^2(V_t - V_l^2)} = \frac{V_l^1(1 - r)}{r(V_t - V_l^1) - x(V_t - V_l^2)}\,, \tag{6}$$

where $r = A_1/A_2$ and $x = V_l^1/V_l^2$. In this study, we take $V_l^1 > V_l^2$, or $x>1$. Therefore, $r>1$. When the solute is under infinite dilution, Eq. (6) gives the Henry's constant of the solute.

The present, the EPICS- and the PRV-methods are very similar. They are all based on solute mass conservation and headspace equilibrium. Furthermore, one can obtain the same equation for calculating the partitioning coefficient, K, with some mathematical manipulations, from these methods. Perhaps, one may argue that these three methods are the same. The differences among these methods are in the experimental approach and data reduction technique. It can be seen that the present method has the advantages of using only two testing solutions, as proposed in the EPICS method, and using the identical sample solution in two vials to conduct two independent measurements, as proposed in the PRV method. By taking the approach of using two testing solutions to conduct only two independent measurements, the present method eliminates unnecessary measurements and calculates the partitioning coefficient, K, by solving a set of two linear equations rather than using linear regression analysis to determine K. By using the identical solution, the present method is not limited to measuring Henry's constant. Furthermore, the solute mass ratio required in the EPICS method is simply the ratio of solution volumes in the two testing vials and can be easily measured with high precision for any samples of unknown solute concentration.

The present study completes the work of Gossett [14] and Ettre et al. [12]. From a mathematical point of view, as we discussed previously, it is sufficient and necessary to solve a VLE problem with two and only two equations (two independent measurements) as in the present method. From a physical point of view, the VLE partitioning coefficient, K, changes with solute concentration, except within the range of infinite dilution in which K can be approximated as a constant, therefore, it is not appropriate to determine K or even Henry's constant on a very strict basis (the concept of infinite dilution is not well-defined physically and mathematically) using two solutions with different concentrations. More importantly, the present study explored the hidden potentials of the EPICS and PRV methods. Through mathematical analysis, we found that the volume ratio of the testing solutions, an independent variable used in all of the three methods, can affect the precision of the methods significantly. Unfortunately, Lincoff and Gossett [13,14] were unable to identify, and Ettre et al. [12] did not study, the effect of the volume ratio of the solutions, x, on the measurement precision of their methods. The volume ratio of the two testing solutions (ten and four) was arbitrarily taken in the studies of Lincoff and Gossett [13,14], respectively, as explained by Gossett [14]. We also found that high precision in measuring large K values (>10) can be achieved by either using a very large solution volume ratio, x (>50) or very small sample volumes in the two testing vials, with a moderate value of x (<5).

3. Experimental

3.1. Chemicals

Methanol and deionized water were used to make solutions of methanol–water. The methanol concentration was about 800 mg/l.

3.2. Apparatus and operation

All measurements were carried out using an HP-7694 automatic headspace sampler and Model HP-6890 capillary gas chromatograph (Hewlett–Packard, Palo Alto, CA, USA). GC conditions: HP-5 capillary column at 30°C; carrier gas, helium (He); flow-rate, 3.8 ml/min. Flame ionization detection (FID) was employed with hydrogen and air flow-rates of 35 and 400 ml/min, respectively. Headspace operating conditions: 25 min with gentle shaking for equilibration of the sample; vial pressurization time, 0.2 min; sample loop fill time, 1.0 min; loop equilibration time, 0.05 min.

The measurement procedure was as follows: Pipette 10 (V_1^1) and 0.05 (V_1^2) ml of the sample solution into two 20 ml vials ($x = V_1^1/V_1^2 = 200$), respectively. Then close the vials and put them into the oven of the headspace sampler. The vial is gently shaken to achieve equilibrium. The vial is then pressurized by helium to create a pressure head to fill the sample loop. The vapor in the sample loop is finally analyzed by GC.

4. Results and discussion

4.1. Precision analysis of the method

We conducted a mathematical precision analysis of Eq. (6), based on the following variance estimation equation:

$$\sigma^2(H^*) = \left(\frac{\partial H^*}{\partial V_1^1}\right)^2 \sigma^2(V_1^1) + \left(\frac{\partial H^*}{\partial r}\right)^2 \sigma^2(r) + \left(\frac{\partial H^*}{\partial x}\right)^2 \sigma^2(x) + \left(\frac{\partial H^*}{\partial V_1^2}\right)^2 \sigma^2(V_1^2) + \left(\frac{\partial H^*}{\partial V_t}\right)^2 \sigma^2(V_t) \quad (7)$$

where the variance of r can be calculated from the variances of the peak areas A_1 and A_2, similar to that of H^*,

$$\sigma^2(r) = \frac{1}{A_2^2}\sigma^2(A_1) + \frac{A_1^2}{A_2^4}\sigma^2(A_2)\,. \quad (8)$$

We conducted replica HSGC measurements in nine testing vials filled with 10 μl (much less than the smallest volume of the smaller sample, i.e., $V_1^2 = 40$ μl, used in this study) of a methanol–water solution to determine the variance of the GC peak

Table 1
List of measurements to determine the variance of GC peak area

Sample number	Measured GC peak area
1	188.2
2	189.3
3	193.2
4	185.4
5	188.9
6	195.7
7	193.0
8	196.3
9	196.5
Mean	191.8
R.S.D.	2.1%

area A. We found that the relative standard deviation (R.S.D.) of nine replica measurements was 2.1%, as listed in Table 1. Based on this experiment, we take $\sigma^2(A_1) = \sigma^2(A_2) = 2.5\%A_1 > 2.5\%A_2$ ($A_1 > A_2$ in this study). We have $\sigma^2(r) = 0.625 \cdot 10^{-3}(r^2\mathrm{H})$ from Eq. (8). The variances of other independent variables were also determined experimentally. We found from experiments that the main contribution to the variance of H^* or K is the r term. By neglecting the contribution from other measurable experimental variables, we have

$$\frac{\sigma^2(H^*)}{(H^*)^2} \approx \frac{(1-x)^2}{(1-r)^4}\left(\frac{V_t}{V_1^1}\right)^2 (H^*)\sigma^2(r). \quad (9)$$

It can be seen from Eq. (9) that the relative variance of the measured partitioning coefficient, K (H^*), is a complex function of the experimental variables, x, K (H^*), and V_1^1 (or V_1^2). Mathematical calculations were carried out to study the precision of the developed method for solution volume ratios, x, ranging from 2 to 1000, with a VLE partitioning coefficient, K, ranging from 2 to 1000, and with $V_1^1 = 10$, 1, 0.1 and 0.05 ml. We found that the volume ratio, x, of the two testing solutions can affect the precision of the method significantly. The calculated results indicate that the relative measurement error increases rapidly with x initially and then reaches an asymptotic value, as shown in Fig. 1, where the volume of the large sample V_1^1 was 10 ml. The predicted experimental errors of Henry's constant of methanol ($H_c = 0.0017$ or $K = 588$) in the methanol–water solution agree with those obtained

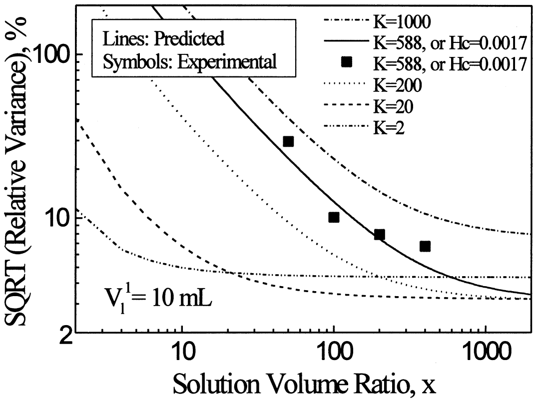

Fig. 1. Analysis of the effect of the solution volume ratio, x, on the relative error in measuring various partitioning coefficients, K values, using the present method with $V_1^1 = 10$ ml.

experimentally through several replica measurements, as shown in Fig. 1. Fig. 1 also indicates that a very large solution volume ratio ($x > 100$) is required to obtain a good measurement of the VLE partitioning coefficient, K, when it is large ($K > 200$). This is because the two separate HSGC measurements of the vapor in the two headspaces will not be significantly different or the ratio of the peak areas, r, is not sufficiently greater than unity (r can be derived from Eq. (6)) to obtain good accuracy when a small difference between the two sample volumes or a small x is used. This precision behavior was also observed by Ettre et al. [12] in their study. Unfortunately, little was done to resolve the problem in their study. The authors proposed to reduce the solute concentration, meaning to alter the measurement system.

Our analysis also indicates that by significantly reducing the sample volumes of both samples, good accuracy can be obtained with a small x for measuring large K values, as shown in Fig. 2a, where the larger sample volume V_1^1 was varied. To obtain good VLE analysis of a system with a very large K (~1000) value of the solute, we can design an experiment using a very large value of x ($x = 1000$) with $V_1^1 = 10$ ml (or $V_1^2 = 10$ μl), or design one using a small value of x ($x = 4$) with $V_1^1 = 100$ μl (or $V_1^2 = 25$ μl), as shown in Figs. 1 and 2a, respectively. The advantage of using small sample sizes and a small solution volume ratio, x, is that the equilibrium time can be reduced significantly during experiments, as we will show later. Our experimental data

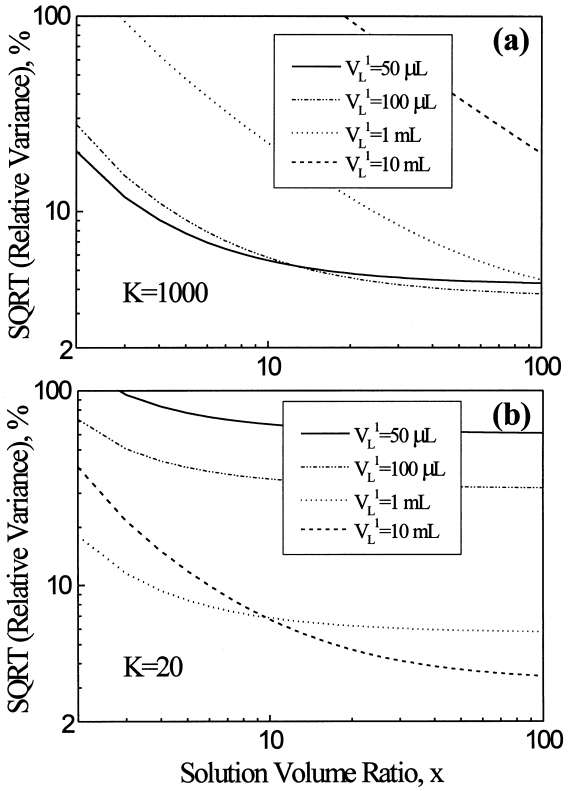

Fig. 2. Analysis of the effect of the sample volume V_1^1 on the relative measurement error at different solution volume ratios, x values. (a) $K=1000$ and (b) $K=220$.

indicate that the sensitivity of the GC measurements will not deteriorate by using small sample sizes to measure very large K values. Table 2 shows the effect of sample size on the measured GC signal (peak area) of the methanol–water solution. The GC peak area was only reduced threefold when the sample size was decreased by three orders of magnitude. A signal level of peak area $A=190$, obtained using the smallest sample size of 10 μl, is well in the range of a good signal-to-noise ratio, as the GC linear response range was $A=0$–2000. The GC signal will drop much faster with a decrease in sample size for systems with smaller K values. However, we found that the system is not suitable for measuring small K values using small sample sizes and a small solution volume ratio, as shown in Fig. 2b. Small K values can be easily and accurately measured with large sample sizes in both of the testing vials using the present-, EPICS- and PRV methods.

Table 2
Effect of sample size on the measured GC signal (peak area) of methanol in water (concentration, 800 mg/l)

Sample size (μl)	Measured GC peak area
10 000	600.1
5 000	598.7
1 000	588.6
500	576.4
100	494.4
50	419.8
40	390.3
30	349.4
20	288.9
10	190.2

4.2. Equilibrium time

The present method is based on the fact that the two solutions in the sample vials have reached a vapor–liquid phase equilibrium. The commercial HP-7694 automatic headspace sampler applies gentle shaking to the sample vial to achieve equilibrium. The time required to obtain equilibrium will not be the same when the volumes of the sample solution in 20-ml vials are different. Using a small sample volume can reduce the equilibrium time for the experiment significantly, as shown in Fig. 3. There-

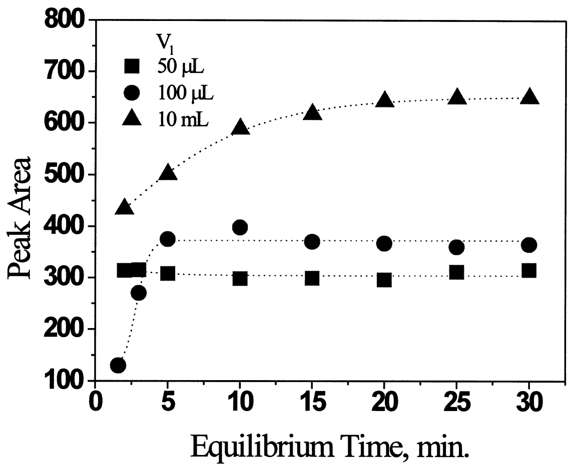

Fig. 3. Effect of solution sample volume on equilibration time.

Table 3
Comparison of the Henry's constant of methanol in water measured using the present method with two different sets of experimental parameters

Experiment	Experimental parameters			Measured Henry's constant, H_c				
	V_1^1 (ml)	V_1^2 (ml)	$x=V_1^1/V_1^2$	T=40°C	T=50°C	T=60°	T=70°C	T=80°C
I	10	0.05	200	0.00042	0.00062	0.00111	0.00171	0.00284
II	0.1	0.04	2.5	0.00052	0.00067	0.00105	0.00169	0.00250

fore, a small sample volume is recommended when using the present method.

4.3. Application of the method

Determination of large values of the VLE partitioning coefficient ($K>200$), such as the Henry's constant of methanol H_c ($=1/K$) in water, for temperatures ranging from 295 to 350 K, is difficult. Indirect techniques are ideal for this type of application because they can eliminate most of the systematic and calibration errors. We conducted two sets of experiments to demonstrate that the present indirect HSGC method can be applied with good precision. We used two completely different sets of experimental parameters $V_1^1=10$ ml and $V_1^2=50$ μl (or $x=V_1^1/V_1^2=200$) and $V_1^1=100$ μl and $V_1^2=40$ μl (or $x=V_1^1/V_1^2=2.5$), respectively, to measure the same quantity of the Henry's constant of methanol, H_c, in water. Identical results were obtained, as shown in Table 3, indicating the validity of our mathematical precision analysis of the method. We averaged the measurements of the Henry constant of methanol from the two sets of experiments to compare with literature data. The data obtained using the present indirect HSGC method showed excellent agreement with those values given in the literature [15–19], as shown in Fig. 4. A linear regression analysis shows that the logarithm of all the data fit to a straight line, with the inverse of temperature, very well, demonstrating the validity and the accuracy of the present method.

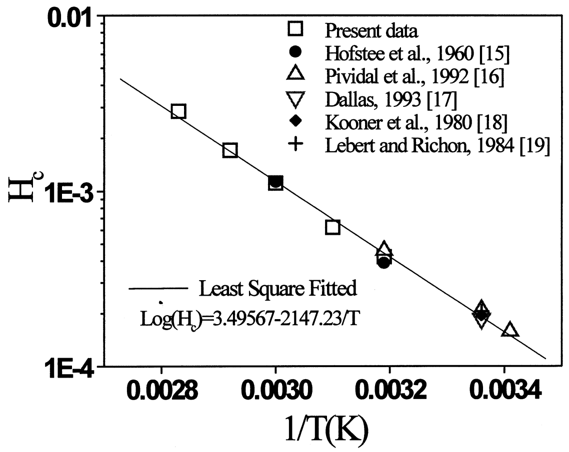

Fig. 4. Temperature effect on methanol Henry's constant and a comparison with literature data.

5. Conclusions

This study completed the work of Lincoff and Gossett [13,14] and Ettre et al. [12] on the development of indirect methods for rapid, automated and precise measurements of vapor–liquid phase equilibrium partitioning coefficients of solutes in any solution using commercial headspace gas chromatography. We derived an indirect HSGC method similar to that of Lincoff and Gossett [13,14] and Ettre et al. [12] that was based on solute mass conservation and headspace equilibrium. We conducted a mathematical precision analysis of the method and found that it can be applied to the measurement of a wide range of VLE partitioning coefficients, K, with excellent accuracy, using different sets of experimental parameters. We identified the volume ratio of the two testing solutions, x, as a key parameter that dictates the accuracy of the present-, EPICS- and PRV methods. Our experimental results show that the methanol Henry's constant in a methanol–water solution obtained using the present method agrees with that in the literature very well. The present method is rapid, automated and does not require that one modify the sample matrix and know the solute concentration in the sample, which has significant importance in industrial, environmental and other practical applications.

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References

[1] D. Mackay, W.Y. Shiu, J. Phys. Chem. Ref. Data, 10 (1981) 1175.
[2] L.H. Turner, Y.C. Chiew, R.C. Ahlert, D.S. Kosson, AIChE J., 42 (1996) 1772.
[3] S.R. Sherman, D.B. Trampe, D.M. Bush, M. Schiller, C.A. Eckert, A.J. Dallas, J. Li, P.W. Carr, Ind. Eng. Chem. Res., 35 (1996) 1044.
[4] T.G. Kieckbusch, C.J. King, J. Chromatogr. Sci., 17 (1979) 273.
[5] A. Hassam, P.W. Carr, Anal. Chem., 57 (1985) 793.
[6] W. Jones, M.J., Egoville, E.O. Strolle, E.S. Dellamonien, J. Chromatogr., 455 (1988) 45.
[7] B. Kolb, C. Welter, C. Bichler, Chromatographia, 34 (1992) 235.
[8] C.A. McAuliffe, Chem. Tech. (1971) 46.
[9] B.V. Ioffe, A.G. Vitenbery, Head-Space Analysis and Related Methods in Gas Chromatography, Wiley, New York, 1984.
[10] R. Guitart, A. Puigdemont, M. Arboix, J. Chromatogr., 491 (1989) 271.
[11] B. Kolb, L.S. Ettre, Chromatographia, 32 (1991) 505.
[12] L.S. Ettre, C. Welter, B. Kolb, Chromatographia, 35 (1993) 73.
[13] A.H. Lincoff, J.M. Gossett, in W. Brutsaert and G.H. Jirka (Editors), Gas Transfer at Water Surfaces, Reidel, Dordrecht, 1984, p. 17.
[14] J.M. Gossett, Environ. Sci. Technol., 21 (1987) 202.
[15] M.T. Hofstee, A. Kwantes, C.W.A. Rijnders, Symp. Dist. Brighton, (1960) 105.
[16] K.A. Pividal, A. Birtigh, S.I. Sandler, J. Chem. Eng. Data, 37 (1992) 484.
[17] A.J. Dallas, Ph.D. Dissertation, University of Minnesota, Minneapolis, MN, 1993.
[18] Z.S. Kooner, R.C. Phutela, D.V. Fenby, Aust. J. Chem., 33 (1980) 9.
[19] A. Lebert, D.J. Richon, J. Agric. Food Chem., 32 (1984) 1156.