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DETERMINATION OF ACTIVITY COEFFICIENTS AT VERY LOW CONCENTRATIONS BY THE INERT GAS STRIPPING METHOD*

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SUMMARY

Based on a theoretical concept of changes in solute concentration brought about by the passage of an inert gas, a measuring apparatus was set up and a saturation vessel devised that alters the equilibrium between the liquid and gaseous phases. The inert gas flow-rate was optimized. Two variants of the experimental procedure were tested on *n*-pentane and *n*-octane. The results obtained on passage of the pure inert gas were within the limits of error of the results obtained by employing pre-saturation.

The proposed method is not too laborious and is easy to perform; on the other hand, the period required for the necessary decrease in concentration is very long (up to several days).

The pre-saturation variant can be used when highly volatile solvents are involved, whereas the other variant has to be used if trace amounts of impurities in the solvent could affect the concentration of the solute in the solution being measured.

INTRODUCTION

Activity coefficients of components at infinite dilution are important thermodynamic quantities used in the characterization of phase equilibria. There are a number of methods (in chromatography they are "static" methods) for the determination of activity coefficients of solutes in finite concentrations; their extrapolation to the concentration limits, however, is usually inaccurate or completely unsuccessful. A common procedure for the determination of the γ^∞ values is the "retention time method" in gas-liquid chromatography (GLC), based on a thermodynamic characterization of the equilibrium between the solute and the solvent in a GLC column.

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Experimental and calculation correlations have been proposed for obtaining the true values of the coefficients from experimental data; however, it is not always possible to evaluate adequately the effect of adsorption on the gas-liquid or liquid-solid interface. From this point of view, the inert gas stripping method¹ appears to be suitable for the determination of the limiting activity coefficients for very low concentrations of the solute, because the solvent surface area to weight ratio is negligible compared with that in a GLC column.

THEORETICAL

In accordance with the general procedure presented elsewhere^{1,2}, relationships between the results of chromatographic analysis of the solute and solvent and the volume of inert gas passed were derived³, based on a thermodynamic description of the solute (1)-solvent(2)-inert gas(3) system.

Balance of the components leaving the solution

The relationship between the instantaneous solution composition and equilibrium gaseous phase can be expressed using Raoult's and Henry's laws (assuming $x_1 \rightarrow 0$, $x_2 \rightarrow 1$, $x_3 \rightarrow 0$):

$$f_1^- = x_1 \gamma_1 f_1^0 \quad (1)$$

$$f_2^- = x_2 f_2^0 \quad (2)$$

$$f_3^- = x_3 H_{3,2} \quad (3)$$

where f_i^- ($i = 1,2,3$) is the fugacity of component i in the system outlet, f_i^0 ($i = 1,2$) is the fugacity of the pure component at the system temperature, γ_1 is activity coefficient of the solute at a given composition and temperature of the liquid phase, $H_{3,2}$ is Henry's constant for inert in pure solvent,

$$x_i = \frac{n_i}{n_1 + n_2 + n_3} \quad (4)$$

($i = 1,2,3$), x_i is the molar fraction of component i in the liquid phase and n_1 , n_2 and n_3 are moles of solute, solvent and dissolved inert gas, respectively, in the solution.

The system fugacity is given approximately as the sum of fugacities of the components according to eqn. 1, 2 and 3:

$$f^- \approx f_1^- + f_2^- + f_3^- \quad (5)$$

and then

$$dn_1^- = x_1 \gamma_1 \cdot \frac{f_1^0}{f^-} \cdot dn^- \quad (6)$$

$$dn_2^- = x_2 \cdot \frac{f_2^0}{f^-} \cdot dn^- \quad (7)$$

where dn_1^- and dn_2^- are infinitesimal masses of solute and solvent leaving the solution simultaneously with dn_3^- moles of inert gas. Further,

$$dn^- = dn_1^- + dn_2^- + dn_3^- \quad (8)$$

From eqns. 6-8 the relationship

$$dn^- = \frac{f^- dn_3^-}{f^- - x_1 \gamma_1 f_1^0 - x_2 f_2^0} \quad (9)$$

can be obtained, which, in combination with eqns. 4 and 6 and eqns. 4 and 7 gives the explicit expression for the instantaneous solution composition and leaving gaseous phase:

$$dn_1^- = \frac{n_1}{n_2} \cdot \gamma_1 \cdot \frac{f_1^0}{f^-} \cdot \frac{dn_3^-}{A} \quad (10)$$

or

$$dn_2^- = \frac{f_1^0}{f^-} \cdot \frac{dn_3^-}{A} \quad (11)$$

where

$$A = 1 - \frac{f_2^0}{f^-} + \left(1 - \gamma_1 \cdot \frac{f_1^0}{f^-}\right) \frac{n_1}{n_2} + \frac{n_3}{n_2} \quad (12)$$

Balance of the components entering the solution from the overall balance

There are two main possibilities: either pure inert gas is used^{1,2} or the inert gas is saturated with solvent vapour so that loss of the solvent is prevented. In view of the assumption of a highly dilute solution, most of the quantities in eqns. 10 and 11 can be regarded³ as independent of concentration and their values approximated by those occurring at the beginning of the measurement. The factor γ_1 in eqn. 12 can be considered as a correlation factor, as the effect of all the terms except $1 - f_2^0/f^-$ on A is virtually negligible.

Passage of pure inert gas

In this instance

$$dn_1 = -dn_1^- \quad (13)$$

$$dn_2 = -dn_2^- \quad (14)$$

$$dn_3^- = dn_3^+ - \frac{f_3^-}{H_{3,2}} \cdot dn_2 \quad (15)$$

where the superscript + refers to entering the solution. Combining eqns. 10 and 11, we obtain

$$d \ln n_1(n_3^+) = \gamma_1 \cdot \frac{f_1^0}{f_2^0} \cdot d \ln n_2(n_3^+) \quad (16)$$

where $n_1(n_3^+)$ and $n_2(n_3^+)$ are functions of the masses of the inert gas that entered the solution during the experiment. The change in the mass of the solute can be obtained fairly accurately by measuring the areas, S_1 , enclosed by the chromatographic elution peaks of the substance; the decrease in the mass of solvent has been described by Burnett². With this arrangement, γ_1 can be expressed as

$$\gamma_1 = \frac{f_2^0}{f_1^0} \left\{ i + \frac{\text{dln } S_1(n_3^+)/S_1(0)}{\text{dln} \left[1 - \frac{1}{n_2(0)} \cdot \frac{f_2^0}{f^-} \cdot \frac{n_3^+}{A - f_2^0/f^- \cdot f_3^-/H_{3,2}} \right]} \right\} \quad (17)$$

where (0) denotes the quantity in question at the beginning of the experiment and (n_3^+) denotes the value after the entry of n_3^+ moles of pure inert gas into the solution.

Passage of inert gas saturated with solvent vapour

The inert gas saturated with solvent vapour is fed into the solution under conditions such that changes in amount of solvent are prevented. There is only one significant difference in the conditions with pre-saturation and the use of a saturation vessel, namely the pressure. The effect of this difference is offset by a corresponding rise in temperature:

$$P_2^0(T^+) = \frac{x_2^-}{x_2^+} \cdot \frac{P^+}{P^-} \cdot P_2^0(T^-); P_2^0(T^+) = >T^+ \quad (18)$$

where + refers to the values in the pre-saturator and - to those in the saturation vessel.

The change in the mass of the solute (eqn. 10), can be found accurately by GLC analysis; the activity coefficient for very low concentration can be written as

$$\gamma_1 = -n_2(0) \cdot \frac{f^-}{f_1^0} \cdot A \cdot \frac{\text{dln } S_1(n_3^+)}{\text{dn}_3^+} \quad (19)$$

EXPERIMENTAL

n-Pentane was obtained from Carlo Erba (Milan, Italy), *n*-octane from VEB Laborchemie (Apolda, G.D.R.) and carbon tetrachloride from Lachema (Brno, Czechoslovakia).

The two variants of the method were tested on the *n*-pentane(1)-*n*-octane(2) system using nitrogen(3) as the inert gas. Each experiment consisted of 20-30 analyses, in which the amount of inert gas passed was read, two or three injections were made in rapid succession and the n_3^+ value was read again and averaged with the preceding one. This sequence was performed approximately ten times. The concentration dependence of γ_{CCl_4} in C_8 was obtained based on analogous procedures.

The experimental data required for the determination of γ^∞ based on eqn. 17 or 19 were measured on the apparatus depicted in Fig. 1. Its basic unit was the saturation vessel (5), depicted in Fig. 2.

The volume of solution measured was approximately 130-140 ml. The coil

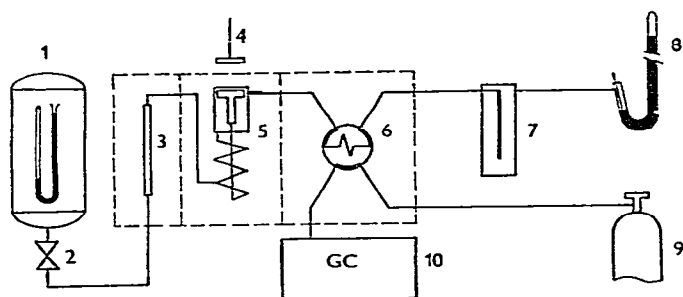


Fig. 1. Apparatus. 1 = Pressure vessel containing the inert gas; 2 = gas flow control; 3 = pre-saturator; 4 = rotating permanent magnet; 5 = saturation vessel; 6 = proportioning valve; 7 = capacity vessel; 8 = manostat; 9 = pressure vessel containing the carrier gas; 10 = gas chromatograph.

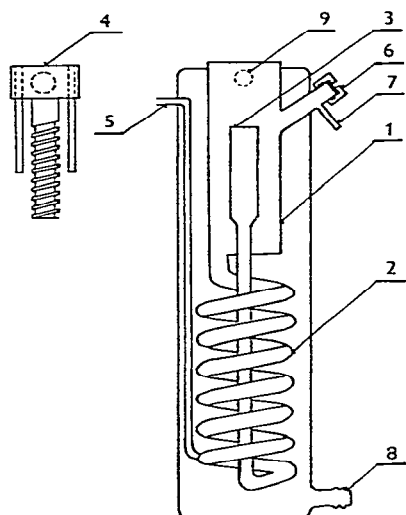


Fig. 2. Saturation vessel. 1 = Open flask; 2 = coil filled with glass beads; 3 = PTFE screw bush; 4 = PTFE screw; 5 = capillary of inert gas inlet; 6 = sampling device; 7 = vapour phase outlet; 8 = thermostated water inlet; 9 = thermostated water outlet.

(I.D. 7 mm) was filled with glass beads 3–3.5 mm in diameter. The circulation of the solution through the coil (0.2 ml/sec) with a counter-flow of the inert gas was provided by a rotating PTFE screw applying a flow-rate of the inert gas such that equilibrium between the liquid and vapour phases could be established.

The inert gas was fed from a pressure vessel (1, Fig. 1) of volume 37.72 l, allowing precise control of the overpressure from 0.01 to 0.19 MPa.

With *n*-pentane the analysis was performed on a Chrom 4 gas chromatograph with a flame-ionization detector (FID). The column dimensions were 3.5 m × 3 mm I.D., the support was Chromaton NAW DMCS (0.125–0.160 mm) wetted with 5 wt. % of Apiezon L, the column temperature was 343.15°K, the carrier gas was nitrogen and the overpressure was 0.06 MPa. In the FID the flow-rates of hydrogen and air were 0.5 and 5 ml/sec, respectively. Analysis of carbon tetrachloride was carried out on a home-made gas chromatograph with a Carlo Erba HT 20 electron-capture

detector. The column dimensions were 2.4 m × 3 mm I.D., the packing was the same as above (0.1–0.125 mm), the column temperature was 338.15°K, and the carrier gas was nitrogen, free from oxygen and water, at a flow-rate of 0.33 ml/sec.

RESULTS AND DISCUSSION

Testing the method

The dependences of $\log S_1(n_3^+)$ on n_3^+ or on $\log(1 - \text{constant} \cdot n_3^+)$ were obtained experimentally (see Tables I and II, respectively), based on 20–30 analyses each. As the assumption of linearity of the dependences proved to be justified, the corresponding straight lines were constructed by applying the least-squares method, the slopes were determined and the error of the slopes was estimated⁴. For the pre-saturation method, the pre-saturator temperatures were calculated by using eqn. 18, which has been proved³ not to introduce a significant error.

TABLE I

LOG S_1 USING VARIANT WITH PRE-SATURATION

System: *n*-pentane (1)–*n*-octane (2)–nitrogen (3). Conditions: $T^- = 293.15^\circ\text{K}$; $P^- = 0.101325$ MPa; $n_2(0) = 0.79506$ mol; $T^+ = 293.43^\circ\text{K}$; $P^+ = 0.103191$ MPa. Average flow-rate of nitrogen =

0.182 ml/sec. Slope: $\frac{d \log S_1(n_3^+)}{dn_3^+} = -0.295622 \pm 0.003529$.

Average value of n^+ (mol)	$\log S_1$		
	1st charge	2nd charge	3rd charge
0	3.56632	3.55712	—
0.20408	3.48671	3.48825	—
0.27612	3.44932	3.45165	3.45309
0.34135	3.43783	3.43953	—
0.60994	3.37262	3.37087	—
0.77952	3.33304	3.32945	3.33126
0.85771	3.29403	3.29296	—
1.09646	3.23629	3.22575	—
1.16767	3.19117	3.20063	3.19526
1.31833	3.13956	3.15254	3.14605
1.38210	3.12613	3.13518	3.13387
1.74945	3.04805	3.02965	—
1.92961	2.98046	2.97823	2.98162

The dependence of the slope per unit amount of the solvent on the flow-rate of the inert gas (Table III) indicates the optimal nitrogen flow-rate to be $4 \cdot 10^{-5}$ – $8 \cdot 10^{-6}$ mol/sec, or 0.1–0.2 ml/sec. The data necessary for the calculation of the γ value from eqn. 17 or 19 were obtained as follows: the fugacities were calculated from the second virial coefficients, the P_i^0 and v_k (molar critical volumes) values were determined according to Voňka *et al.*⁵, the B_{ii} (virial coefficient) values for the alkanes and CCl_4 were calculated according to McGlashan and Potter⁶ and for nitrogen the value was estimated according to Brewer and Vaughn⁷; $B_{ij} \approx (B_{ii} + B_{jj})^{1/2}$; $H_{3,2}$ was assigned the approximate value 77.4 MPa (ref. 8). The errors in the determination of $f_{\text{C}_3}^0$, $f_{\text{C}_8}^0$, $f_{\text{CCl}_4}^0$ and f^- were 0.85, 2.5, 0.2 and 0.21 %, respectively.

TABLE II

LOG S_1 USING VARIANT WITHOUT PRE-SATURATION

System: *n*-pentane (1)–*n*-octane (2)–nitrogen (3). Conditions: $T^- = 293.15^\circ\text{K}$; $P^- = 0.101325 \text{ MPa}$; $n_2(0) = 0.82268 \text{ mol}$. Average flow-rate of nitrogen = 0.163 ml/sec.

$$\text{Slope: } \frac{d \log S_1(n_3^+)}{d \log \left[1 - \frac{1}{n_2(0)} \cdot \frac{f_2^0}{f^-} \cdot \frac{n_3^+}{A - \frac{f_2^0}{f^-} \cdot \frac{f_3^-}{H_{3,2}}} \right]} = 40.8361 \pm 0.3287.$$

Average value of $\log \left[1 - \frac{1}{n_2(0)} \cdot \frac{f_2^0}{f^-} \cdot \frac{n_3^+}{A - \frac{f_2^0}{f^-} \cdot \frac{f_3^-}{H_{3,2}}} \right]$	$\log S_1$		
	1st charge	2nd charge	3rd charge
0	3.35027	3.34982	—
−0.000342	3.33143	3.33085	3.33062
−0.000522	3.32163	3.32111	3.32330
−0.000950	3.30442	3.30492	3.30527
−0.004289	3.17162	3.17280	3.17223
−0.004355	3.15770	3.16125	3.15995
−0.005543	3.12368	3.12188	—
−0.005587	3.11878	3.11633	3.11585
−0.008285	3.01063	3.00556	3.00109

TABLE III

DEPENDENCE OF SLOPE ON INERT GAS FLOW-RATE

System: *n*-pentane (1)–*n*-octane (2)–nitrogen (3). Experiment temperature, 293.15°K ; pre-saturator temperature, 293.43°K ; experiment pressure, 0.101325 MPa.

Nitrogen flow-rate (ml/sec)	$n_2(0) \cdot \frac{d \log S_1}{dn_3^+}$ (mol)
0.097	−0.23452
0.182	−0.23504
0.200	−0.23536
0.253	−0.23365
0.290	−0.21615
0.385	−0.16900

The error of the determination of $n_2(0)$ is negligible and that of the determination of A is about 0.05%. For an analysis of the errors, the dependences of the slope per unit amount of solvent on pressure and temperature were established experimentally by applying the optimal flow-rate (Tables IV and V, respectively). For absolute errors with measurements of temperature of $\Delta T \approx 0.02^\circ\text{K}$ and pressure of $\Delta P \approx 70 \text{ Pa}$, the inaccuracy in the temperature measurement leads to a relative error of 0.068% and the inaccuracy in the pressure measurement and stabilization results in a relative error of 0.073%.

Based on the results of measurements given in Tables I and II, the values of the activity coefficients were calculated for *n*-pentane and *n*-octane at 293.15°K and

TABLE IV

DEPENDENCE OF SLOPE ON THE SATURATOR PRESSURE

System: *n*-pentane (1)–*n*-octane (2)–nitrogen (3). Experiment temperature, 293.15°K; pre-saturator temperature, 293.43°K; flow-rate of N₂, 0.1–0.2 ml/sec.

Saturator pressure (kPa)	$n_2(0) \cdot \frac{d \log S_1}{dn_3^+}$ (mol)
100.0	–0.23895
101.325	–0.23504
103.3	–0.23052

TABLE V

DEPENDENCE OF SLOPE ON THE EXPERIMENT TEMPERATURE

System: *n*-pentane (1)–*n*-octane (2)–nitrogen (3). Experiment pressure, 0.101325 MPa; flow-rate of N₂, 0.1–0.2 ml/sec.

Pre-saturator temperature (°K)	Saturator temperature (°K)	$n_2(0) \cdot \frac{d \log S_1}{dn_3^+}$ (mol)
288.47	288.15	–0.19513
290.93	290.65	–0.21458
293.43	292.15	–0.23504
295.94	295.65	–0.25754
298.45	298.15	–0.28410

a mean molar fraction of $x_1 = 0.0001$. The error was derived from the statistical error of the slope and the errors of the various variables and effects. For the procedure without pre-saturation $\gamma_1 \approx 1.003 \pm 0.042$ and for the procedure with pre-saturation $\gamma_1 = 0.982 \pm 0.023$. These results are consistent with the assumed behaviour of the *n*-pentane–*n*-octane system; a value of 0.99 has been found⁹ at 303.15°K. Thus it is possible to employ the procedure in question for the determination of γ at very low concentrations.

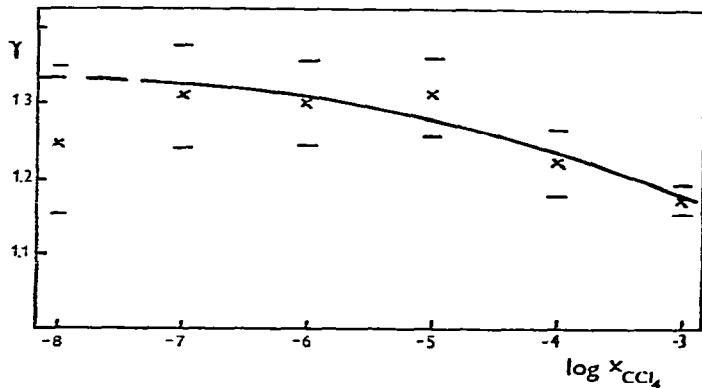


Fig. 3. Dependence of γ_{CCl_4} on CCl₄ concentration.

Concentration dependence of γ_{CCl_4}

The above procedures were used to obtain the γ_{CCl_4} values in *n*-octane at six different concentrations of carbon tetrachloride. When $x_{\text{CCl}_4} = 10^{-3}$ the method with pre-saturation was applied; the other systems were studied by using the variant without pre-saturation. The liquid phase was analysed and the dependence of $\log S_1(n_3^+)/S_1(0)$ on $\log(1 - \text{constant} \cdot n_3^+)$ followed, where $S_1(0)$ is the peak area of the standard injected in succession (solution of carbon tetrachloride in *n*-octane of the same concentration as that of the solution measured at the beginning of the experiment). The errors of the individual measurements were determined as for the *n*-pentane-*n*-octane system and are plotted in Fig. 3. Extrapolation leads to an estimate of the limiting activity coefficient of carbon tetrachloride in *n*-octane at 293.15°K of $\gamma_{\text{CCl}_4}^\infty = 1.34$.

REFERENCES

- 1 J. C. Leroi, J. C. Masson, H. Renon, J. F. Fabries and H. Sannier, *Ind. Eng. Chem., Process Des. Develop.*, 16 (1977) 139.
- 2 M. G. Burnett, *Anal. Chem.*, 35 (1963) 1567.
- 3 B. Doležal, *Thesis*, Institute of Chemical Technology, Prague, 1980.
- 4 D. J. Hudson, *Statistics*, Geneva, 1964.
- 5 P. Voňka, M. Zábranský and J. P. Novák, *Chem. Prům.*, 30 (1980) 2.
- 6 M. L. McGlashan and D. J. B. Potter, *Proc. R. Soc. London, Ser. A*, 267 (1962) 478.
- 7 J. Brewer and G. W. Vaugh, *J. Chem. Phys.*, 50 (1969) 2960.
- 8 E. S. Thomsen and J. Ch. Gjaldbaek, *Acta Chem. Scand.*, 17 (1963) 127.
- 9 S. Dal Nogare and R. S. Juvet, *Gazo-židkostnaja Khromatografia*, Nēdra, Leningrad, 1966.