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DETERMINATION OF ACTIVITY COEFFICIENTS OF BINARY LIQUIDS BY CAPILLARY GAS CHROMATOGRAPHY WITH THERMAL DESORPTION MODULATION FOR DIRECT HEADSPACE SAMPLING

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SUMMARY

Activity coefficients of the binary liquid mixtures benzene–toluene and acetone–chloroform were determined using thermal desorption modulation for direct headspace sampling into a capillary gas chromatograph. A thermal desorption modulator is a short, heated section at the head of the column. An electrical current pulse applied to a thin conductive film heats the modulator section and the stationary phase within it, releasing any retained substances as a concentration pulse which flows into the column. The modulator acts like an automatic and highly reproducible small-volume injector for a continuously flowing sample stream. Short-term relative standard deviations obtained using this technique are approximately 2%.

INTRODUCTION

Classical methods for the determination of the activity coefficients of volatile liquids in solution are laborious and time-consuming[1]. In addition, their accuracies and precisions are not as good as desired[2]. Gas–liquid chromatography has been used to determine the activity coefficients of volatile solutions at infinite dilution in the stationary phase in a column[3–7]. This method is faster and simpler than classical methods, but is can only be applied to binary systems in which the solvent is a gas–liquid chromatographic stationary phase and the solute is near infinite dilution. Arnikar *et al.*[8] proposed a headspace sampling method which can be used with a variety of solvent–solute combinations and for a wide range of concentrations. However, the instrumentation is complicated. A simplified procedure was employed by Barrett and Stewart[9], but the vapor injection and difficult temperature control make the method not very precise or accurate.

The increasing use of headspace methods in aroma analysis has already led to the development of many new headspace sampling techniques to circumvent problems with solvent extraction or distillation methods. Basically, there are two kinds of

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headspace sampling, indirect (combined sampling and enrichment by condensation or sorption) and direct[10]. For example, Curvers *et al.*[11] investigated the possibilities and limitations of dynamic headspace sampling as a preconcentration technique for the trace analysis of organics. Jentzsch *et al.*[12] introduced a headspace sample directly into the chromatographic column by pressurizing the headspace vessel for quantitative gas chromatographic (GC) analysis.

Multiplex chromatography can directly accept large volume samples provided that the bulk of the sample is suitable for use as a mobile phase[13]. This technique has several advantages over conventional chromatography, including an improved detection limit for samples of low concentration. The most important advantage for headspace samples is the ease and high precision of sample introduction. For example, Koel *et al.*[14] used the technique to follow the sample concentration from an exponential dilution flask.

Thermal desorption modulation has been used with multiplex gas chromatography for direct sampling of the headspace above a plastic sample[13]. We have now applied the same technique to measure the activity coefficients of binary liquids. Two systems, benzene–toluene and acetone–chloroform, were investigated. The method is simple, highly reproducible and easily computer automated.

EXPERIMENTAL

Apparatus

Experiments were performed using a Perkin-Elmer Model 3920 gas chromatograph with a flame ionization detector for the benzene–toluene system and a Varian Model 2700 gas chromatograph with an electron-capture detector for the acetone–chloroform system. The instrument design is shown in Fig. 1. The injection port was modified to hold the sampler as shown in Fig. 2. The laboratory computer system has been described previously[13]. The analytical column was a Supelcowax 10 (Supelco, Bellefonte, PA, U.S.A.) fused-silica open-tubular column (25.0 m × 0.250 mm I.D.) with a film thickness of 0.25 μm. The modulator was prepared by applying an electrically conductive paint to an 8-cm section at the head of the column. The modulator's resistance was 1.6 Ω. Its design and construction have been described previously[13]. The modulator was outside the oven with only enough of it extending

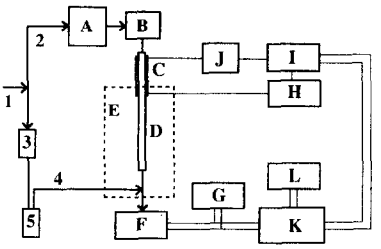

Fig. 1. Schematic diagram of the capillary GC instrument including thermal desorption modulator. A = Sample holder; B = manometer; C = thermal desorption modulator; D = column; E = oven; F = detector (flame ionization or electron-capture); G = recorder; H = power supply; I = optically coupled switch; J = resistor; K = computer; L = plotter; 1 = nitrogen gas supply; 2 = carrier gas; 3 = flow switch; 4 = make-up gas; 5 = flow controller.

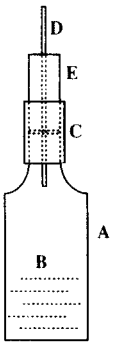

Fig. 2. Sample holder. A = Glass tube; B = sample; C = rubber tube connector; D = capillary tube; E = shrinkable tubing.

into the heated zone to avoid the presence of any cold stationary phase between the modulator and column. A U-shaped mercury manometer was placed between the column and the sampler to monitor the sample pressure. The pressures of all samples were equal. The computer controlled the modulator current from a 40 V d.c. power supply using an OPTO 22 Model ODC5P optically coupled switch.

Materials

Analytical-reagent grade benzene, toluene, acetone and chloroform were purchased from Fisher Scientific. Nitrogen, helium and hydrogen were of prepurified grade from Air Products.

Procedures

Liquid samples were placed into a 4.0-mm diameter glass tube. A 2.0 cm × 250 μm I.D. capillary was connected to the liquid sample holder as shown in Fig. 2. The ratio of the inside diameters of the reservoir glass tube and the capillary was large enough for the vapor concentration gradient along the reservoir to be neglected. A capped reservoir containing a particular molar fraction mixture was equilibriated in the injector for 30 min, then its cap was removed, the capillary restrictor installed and the whole sampler placed quickly in the injector.

A series of modulation pulse chromatograms were obtained from headspace gases above liquid mixtures with molar fractions varying from 0 to 1. Either a recorder connected directly to the gas chromatograph or a plotter connected to the computer could be used to record chromatograms.

Conventional injection chromatograms were also obtained. The recorder chart speed (1.0 cm/min) was much lower than that used in our method (2.5 cm/min). The injection splitting ratio was 1:10. Other chromatographic conditions were as specified in Fig. 3. A series of solutions with benzene molar fractions from 0 to 1 were placed in septum-capped bottles, which were then placed into an oven at 50°C for 40 min. A small vent needle was inserted through each septum to allow all samples to return to atmospheric pressure. The vent needle was removed and a syringe inserted through the septum. Pumping the syringe slowly ten times promoted mixing of the vapors. A 5-μl headspace sample was then withdrawn and injected through the injection port as soon as possible. A series of conventional chromatograms were thus obtained.

RESULTS AND DISCUSSION

Fig. 3 is a typical chromatogram obtained from a series of modulation pulses generated by computer. From the peak heights of components in the solution and the pure states, activity coefficients were calculated over the whole concentration range.

The activity coefficients a_A and a_B of substances A and B in a solution are $a_A = f_A/f_A^0$ and $a_B = f_B/f_B^0$, where f_A and f_B are the fugacities of components A and B in solution and f_A^0 and f_B^0 are the fugacities of the pure components A and B. If the vapor pressures of A and B are low, one can assume that the law of ideal gases applies and the fugacities are equal to the presures, and therefore $a_A = p_A/p_A^0$ and $a_B = p_B/p_B^0$, or $r_A x_A = p_A/p_A^0$ and $r_B x_B = p_B/p_B^0$, where r_A and r_B are the activity coefficients of A and B, x_A and x_B are molar fractions of A and B in solution, p_A *and* p_B are the partial pressures of the components in equilibrium with the solution and p_A^0 and p_B^0 are saturated vapor presures of the A and B in the pure state.

If we take the saturated vapors at the same volume and temperature and assume that peak height is proportional to concentration, then peak height is proportional to vapor pressure. Hence $p_A/p_A^0 = h_A/h_A^0$, $p_B/p_B^0 = h_B/h_B^0$, $r_A = h_A/x_A h_A^0$ and $r_B = h_B/x_B h_B^0$, where h_A and h_B are the peak heights of the vapors of A and B in equilibrium with the solution and h_A^0 and h_B^0 are the peak heights of the vapors of A and B in equilibrium with pure liquids A and B.

It is difficult to inject a desired volume of vapor into a GC column precisely, especially a capillary column. However, it is easy to effect precise sample introduction using a thermal desorption modulator.

Repeated modulation pulses give almost constant peak heights for the vapors of components A and B in equilibrium with their solution at each molar fraction. Only five pairs of peaks were averaged to calculate the results in Table I. It is possible to improve the precision by averaging more pulses if the experiment is run for a longer time. The variation due to sample introduction through the modulator appears to be random and can be eliminated or reduced by signal averaging. Signal averaging by repeated pulsing of the modulator is convenient and reproducible using thermal desorption modulators controlled by a computer. Signal averaging by conventional GC, however, is diffucult and of poor reproducibility.

Repeated pulsing of the modulator is very simple, requiring no external devices or extra operations to transfer a very small volume into the capillary GC column. The modulator continuously samples the concentration of the headspace vapor analytes in

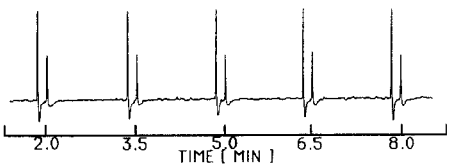

Fig. 3. Typical chromatogram obtained using the thermal desorption modulator for direct headspace sampling. Molar fraction of benzene, 0.60; data acquisition rate, 4 Hz; modulation pulse duration, 120 ms; pulse interval, 90 s; carrier gas flow-rate, 1.6 ml/min; detector make-up flow-rate, 27.0 ml/min; sample holder temperature, 50°C; column temperature, 120°C; detector temperature, 250°C; recorder chart speed, 2.5 cm/min.

TABLE I

ACTIVITY COEFFICIENTS IN BENZENE–TOLUENE BY THERMAL DESORPTION MODULATOR INPUT CAPILLARY GC

Molar fraction		*Mean peak height (mm)*		*R.S.D. (%)*		*Activity coefficient*	
x_A	x_B	*A*	*B*			r_A	r_B
1.00	1.00	53.2		0.2			
0.80	0.20	47.4	11.1	0.2	1.0	1.11	1.38
0.60	0.40	38.2	19.2	0.5	1.1	1.20	1.19
0.40	0.60	28.4	27.0	0.9	0.8	1.33	1.12
0.20	0.80	15.0	34.2	1.5	0.7	1.41	1.06
0.00	1.00		40.2		0.6		
Average				0.7	0.8		

a flowing stream. Once the controlling parameters have been set, the process can run automatically.

Fig. 3 shows that the peaks are different in shape to those obtained with conventional GC. First a positive peak is observed, followed by a negative peak or vacancy. Together they look like the derivative of a conventional chromatogram. The positive peaks are due to desorption of analyte from the modulator stationary phase on heating, and the vacancies are due to readsorption of fresh analyte on the stationary phase on cooling the modulator.

The baseline of the modulator-generated chromatogram is determined by the steady-state sample concentrations, not zero concentration. Concentrations above the steady state are represented by positive peaks whereas concentrations below the steady state are vacancies. Some of the baseline noise is due to the constant bleeding of analyte through the detector[15].

The peaks are very sharp even though the recorder chart speed is faster than that used in conventional injection GC (2.5 *vs.* 1.0 cm/min). This modulation technique generates very sharp injections and is limited by band broadening in the column whereas our manual injection technique (split injection) generates broader peaks.

Sufficient time must be allowed between modulation pulses for the modulator to return to its initial state. Generally, the higher the capacity factor of the sample in the modulator, the longer the pulse interval should be because it will take a longer time to refill the modulator after each thermal desorption pulse. The 90-s repetition period in Fig. 3 is substantially longer than this required refill time. An improvement in signal averaging efficiency could be obtained by decreasing this time period.

The results obtained using this technique are in good agreement with those obtained using the conventional GC method. They are presented in Tables I, II and III for comparison. There are some differences in the activity coefficients of the acetone–chloroform system because the temperature used in our work (50°C) was different from that cited in the literature (35°C)[16,17].

The short-term relative standard deviation (R.S.D.) is often better than 1%, as in Tables I and III, but cannot be relied upon to be better than about 2%. Our syringe injection method will not give results with an R.S.D. better than about 4%.

TABLE II

ACTIVITY COEFFICIENTS IN BENZENE–TOLUENE BY CONVENTIONAL INJECTION CAPILLARY GC

Molar fraction		*Mean peak height (mm)*		*R.S.D. (%)*		*Activity coefficient*	
x_A	x_B	*A*	*B*			r_A	r_B
1.00	0.00	54.6		3.5			
0.80	0.20	50.2	11.3	3.8	4.5	1.15	1.36
0.60	0.40	40.0	19.3	3.2	4.1	1.22	1.17
0.40	0.60	28.7	27.0	4.5	2.4	1.30	1.09
0.20	0.80	15.5	34.5	3.0	3.3	1.42	1.04
0.00	1.00		41.4		3.8		
Average				3.6	3.6		

TABLE III

ACTIVITY COEFFICIENTS IN ACETONE–CHLOROFORM WITH THERMAL DESORPTION MODULAR INPUT

Molar fraction		*Mean peak height (mm)*		*R.S.D. (%)*		*Activity coefficient*[a]	
x_A	x_B	*A*	*B*			r_A	r_B
1.00	0.00	22.1		0.3			
0.80	0.20	17.3	4.9	1.2	1.8	0.98 (0.97)	0.65 (0.63)
0.67	0.33	13.3	9.0	1.2	1.0	0.90 (0.93)	0.74 (0.71)
0.50	0.50	9.0	15.0	1.0	0.9	0.81 (0.84)	0.81 (0.78)
0.33	0.67	5.1	19.2	1.7	0.5	0.70 (0.70)	0.79 (0.83)
0.20	0.80	2.8	27.4	3.6	1.6	0.63 (0.62)	0.93 (0.93)
0.00	1.00		37.0		0.4		
Average				1.5	1.0		

[a] Values from ref. 16 in parentheses.

Determinations run on separate days still have a 2% R.S.D. using the modulator sample input technique, and the R.S.D. increase further when determinations are run on separate days using the syringe injection technique.

This method should be useful for measuring the activity coefficients of other solutions or for measuring other solution parameters such as partition coefficients and enthalpy changes. Reaction kinetics can be investigated by monitoring the effluent from a flow-through micro-reactor. Also, it should be applicable to reaction gas chromatography using a thermal desorption modulator as a micro-reactor and to catalytic gas chromatography using a catalyst as an absorbent within a modulator.

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