Dual vapor and liquid injector for gas chromatography

Labib Ghaoui*, L. Shayne Green

Analytical Sciences, Building 1897B, The Dow Chemical Company, Midland, MI 48667, USA

Abstract

Binary vapor–liquid equilibrium (VLE) data are used in designing process equipment for distillation, extraction, stripping, or decantation. Experimental determinations of VLE data require analyses of vapor and liquid from a binary liquid mixture equilibrated at a specific temperature. A large amount of reliable VLE data can be obtained by using a headspace analyzer with a gas chromatograph. The headspace analyzer is rugged and reproducible, and the analyzer automatically samples the gas phase. The liquid phase is most often manually sampled by insertion of a needle into a heated headspace vial's septum followed by collection of the liquid in a syringe. Representative liquid samples must be collected and analyzed, and safety precautions must be used whenever sampling hot, toxic samples.

A dual sampling system has been developed to automatically sample and inject both headspace and liquid phases from a binary mixture. The system is based on a modification to a Hewlett-Packard 19395A headspace analyzer. The instrument was evaluated with a standard binary VLE system of cyclohexane–n-heptane and the data were found to be consistent with data obtained with a Hewlett-Packard headspace analyzer using conventional procedures.

1. Introduction

A significant amount of process engineering involves designing separation processes such as distillation, extraction, stripping, or decantation. Process engineers avoid any undersizing and oversizing of the process equipment by using phase equilibria data for binary or multicomponent mixtures. Both undersizing and oversizing can be costly for a separation process. One of the most common process separations of liquid mixtures is through distillation. Quantitative

understanding of vapor–liquid equilibria in multicomponent mixtures is required for distillation and can be obtained from liquid-phase activity coefficients as a function of liquid concentration and temperature. Equipment design can thus be optimized using vapor–liquid equilibrium (VLE) data. A comprehensive description of the thermodynamic equation and parameters and the mathematical relationships among these equations have been previously described [1–3]. The relative volatility or separation factor of a binary mixture is calculated from the vapor and liquid concentration data of a binary mixture and related back to activity

* Corresponding author.

coefficients. The equation used to calculate relative volatility is

$$RV = \frac{Y_1/Y_2}{X_1/X_2} \tag{1}$$

where RV is the relative volatility, Y_1 is the mol fraction of the light component in the vapor, Y_2 is the mol fraction of the heavy component in the vapor, X_1 is the mol fraction of the light component in the liquid and X_2 is the mol fraction of the heavy component in the liquid. This equation estimates the ability to separate the components in the mixture.

Several techniques [4] have been developed for obtaining experimental VLE data. A common technique used is headspace gas chromatography (GC), which was suggested by Wichterle and Hala [5]. VLE studies of binary mixtures using static headspace gas chromatography are carried out by preparing various concentrations of the binary mixture in sealed fixed-capacity containers and equilibrating the mixtures at a predetermined temperature. After equilibration, the vapor phase is then sampled either manually or through an automated headspace analyzer and then analyzed by GC. After all the vapor samples have been analyzed, the liquid phase is then sampled while the mixtures are at their equilibration temperature. The liquid samples are analyzed off-line using GC conditions that are similar to the vapor conditions. A more thorough description of static headspace is described in Refs. [1,6-9]. Calculation of mol percent from the prepared mass percent will be adequate in most cases. However, there are certain examples where the liquid concentrations will change because of the relative volatility of the components of interest and the liquid analysis will give the most accurate data.

Sampling of the vapor phase and GC analysis are fully automated using commercially available headspace analyzers in conjunction with a gas chromatograph. Although the injection and analysis of the liquid phase by GC are automated through the use of liquid autosamplers, the liquid sample collection is not automated. The liquid phase must be transferred into liquid autosampler vials, while still at an elevated temperature. Manually transferring of the hot chemical mixture subjects the analyst to potential exposure of volatile chemicals. Also, sampling of the liquid could be a source of error in the VLE data. In some instances, sampling may result in a non-representative sample being collected because of disturbances in the equilibrium and loss of vapor from the previous vapor sampling due to an unsealed septum. The sample composition and homogeneity can also change in the syringe by crystallization or flash evaporation of a component. All these factors could result in collection of a non-representative liquid sample.

In order to completely automate the experimental part of the VLE studies, a dual injector capable of simultaneously injecting vapor and liquid phases from the same vial into two equivalent columns has been constructed. The new system has all the advantage described earlier. In addition, the analysis time is reduced by more than half, because the data for the vapor and liquid phase are generated at the same time and there is no sample transfer operation.

2. Experimental

2.1. Instrumentation

The automated dual injection system is based upon a modification of an HP19395A headspace analyzer. The device is programmed through a data system (PE Nelson, Access*Chrom Data System) as well as the headspace analyzer to synchronize the dual injection. A schematic diagram of the system is shown in Fig. 1. The original air cylinder that is responsible for the needle movement was replaced by another air cylinder (A) that has a longer shaft (2 cm longer than the original one). The air cylinder was obtained from Lyn-Act Manufacturing Corp., IL, USA, and was mounted on the original bracket with longer spacers (25 mm long). The cylinder was controlled using the original electronics of the headspace analyzer. A modified needle joint (B) was constructed with two internal grooves to fit two needles of different
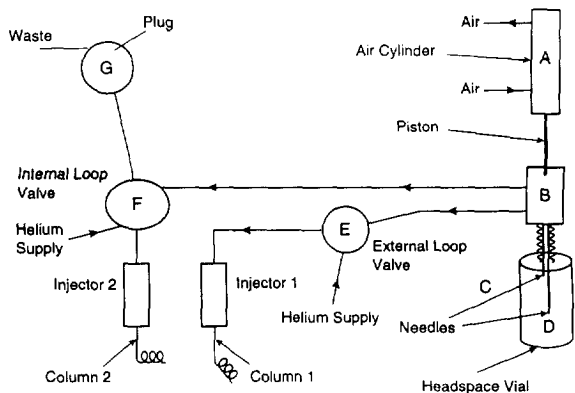
Fig. 1. Schematic diagram of the dual-needle injector.

lengths. One needle allows for vapor sampling and vial pressurizing (C), and the other allows for liquid sampling (D). Fig. 2 illustrates the sampling set-up at an expanded scale. The two needles were housed in a stainless-steel cylinder similar to the original one, but with a larger hole to accommodate the two needles. The needles were obtained in 30 cm long from Hamilton, Reno, NV, USA. The short needle (C) is a 20-gauge side-port needle with a length of 71 mm from the needle joint (B). The longer needle
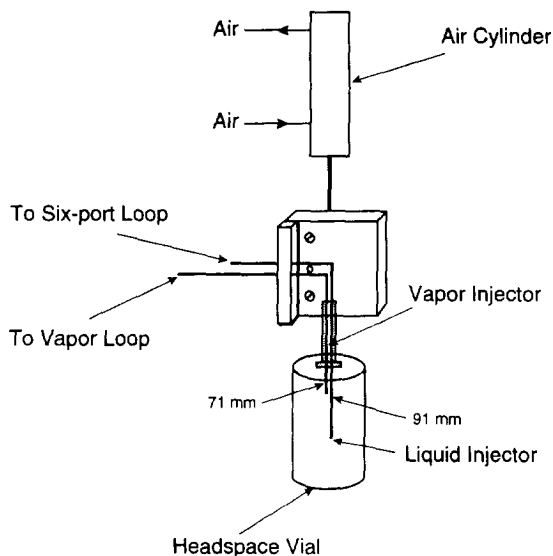
(D) is a 22-gauge sharp point needle with 91 mm length from the needle joint (B). The needle used in vapor sampling was connected via a PTFE tube to the headspace unit's original sampling valve (E), which, in turn, was connected to injector 1. This PTFE connection was changed later to a low dead volume connection from Valco, Houston, TX, USA. The needle used in liquid sampling was connected to a heated transfer line, via a low-dead-volume connector. The transfer line was connected to the sample port of an internal 4-port sampling valve (F) with 0.5-μl volume internal loop. Heating of the transfer line was achieved by passing it through a 60 cm length of copper tube that was wrapped with heat tape and insulation. The temperatures of the transfer line and sampling valve were electronically controlled and monitored with thermocouples. The liquid transfer line, sampling valve, and oil bath for heating the sample vial can be independently controlled at the same or different temperatures up to 150°C. The column port of the sampling valve was connected to the injector with a short length of stainless-steel needle, and the carrier gas port was connected to a helium supply line. The carrier gas flow was controlled by a flow controller. The waste port of the sampling valve was connected to a 6-port switching valve (G). One port of the switching valve was used to plug the waste line and the other was used for collection of liquid in a waste container. The sampling and switching valves were air actuated and electronically controlled using the PE Nelson data acquisition system.

Vapor sampling was controlled by the headspace analyzer's electronics. Sampling of the vapor was performed prior to liquid sampling. During vapor sampling, the waste line of the sampling valve (F) was plugged by the 6-port switching valve (G). After the vapor was injected, the headspace instrument was programmed to pressurize the vial. Simultaneously, the external valve (G) was switched to allow liquid to flow through the sample loop and into the waste container. When a representative liquid sample had been collected, the sample loop was switched into the carrier gas stream, which

Fig. 2. Blow-up diagram of the vapor and liquid sampling set-up.

transferred the sample to the injector. After the liquid was injected, the waste line was plugged (G), the sample loop switched back into the collect position (F), and the needles were removed by the air cylinder (A) from the sample bottle. The sampling system was ready for the next sample analysis.

The gas chromatograph was an HP5890 series II equipped with flame ionization detection (FID) and thermal conductivity detection (TCD) system. FID was used with the liquid injection and TCD was used with the vapor injection. Two different detectors were used because of the GC configuration we had at the time and not because of any technical merits. Two identical detectors will give similar performance. Two 30 m × 0.32 mm I.D., 5 μm 5% CP-SIL-8CB columns (Chrompack) were installed in the two injectors of the gas chromatograph. The sample was introduced into a split injector (injector 1) on column 1. The liquid sample was introduced into the split injector (injector 2) on column 2.

Table 1
Sequence of events for the headspace analyzer

Method 1	Equilibration time	20 min
	Vent	70 s
	Equilibrate	5 s
	Pressurize	60 s
	Equilibrate	30 s
	Vent	70 s
	Pressurize	60 s
Method 2	Equilibration time	20 min
	Vent	5 s
	Equilibrate	5 s
	Vent	5 s
	Equilibrate	5 s
	Inject	60 s
	Pressurize	62 s
Bath temperature		75°C
Loop/valve temperature	Vapor loop	95°C
	Liquid loop	75°C
Loop volume	Vapor loop	1 ml
	Liquid loop	0.5 μl
Transfer line temperature	Vapor	150°C
	Liquid	75°C

2.2. VLE studies

Eight binary mixtures were prepared from HPLC-grade cyclohexane and heptane (Fisher Scientific) with % (w/w) values that ranged from 5 to 95% cyclohexane. Results were obtained as area% values and were assumed to be equivalent to % (w/w) values. Calibration curves were generated for both components. The GC oven was programmed from 100 to 150°C at 3°C/min with an initial hold of 1 min. Both injectors and detectors were held at 250 and 280°C, respectively. Similar flow-rates were allowed into both columns. Split flows from the liquid and vapor injections were 50 and 200 ml/min, respectively. The range for both signals, TCD and FID, was set to 6. The sequence of events for the headspace analyzer during the sampling and injection process are shown in Table 1.

3. Results and discussion

The quality of experimental VLE data is very dependent on the proper use of the headspace equipment and the manual collection of a representative liquid sample for off-line GC analysis. An automated dual injection headspace VLE system was constructed with one short needle and one long needle to perform vapor and liquid injections from the same vial (Fig. 1) to overcome the problems described in the Introduction section about sampling vapor and liquid phases. The dual injector automatically samples the liquid phase after the vapor phase sampling is complete, eliminates manual sampling of hot solutions, and decreases the analysis time by more than half. The system is limited to liquids of low viscosity because the liquid solution is transferred to the valve injector through a transfer line. The current design requires sample sizes of approximately 4–5 ml. This is not a problem for typical VLE studies because we most often study binary mixtures that consist of commercially available reagents or the components are available in large quantities. Because of the design of the sampling system, liquid injection

occurs 1-2 min after the vapor injection. This does not pose any problem with isothermal separations. The temperature program can be modified with a 2-3-min initial hold time to reduce or eliminate any problems that might occur with programmed runs. Evaluation of the dual sampling system involved a chromatographic evaluation of the performance of liquid injection and determination of VLE data for a standard binary mixture.

3.1. Evaluation of liquid sampling system

Liquid injections using a loop injector are used routinely in on-line analysis where feed material from reactors is transferred to a loop injector and fed into the column directly. The combination of this injection technique with the vapor injection technique makes this a unique system for situations where the data from the vapor phase and liquid phase are needed. Due to the 90-cm transfer line and the valve injection of liquid samples, carry-over effects from consecutive runs was an important aspect of the evaluation. A wash solvent can be used between injections or a 2-ml aliquot of the sample can purge the transfer line and the loop injector before the sample is injected. This requires a large sample size. The length of the needles and the vial size restricted use of a smaller sample size. Fig. 3 shows the difference in carry-over effect noticed for an acetonitrile–chlorobenzene sample subjected to different helium purging times. The 0.75- and 1-min purging times (corresponding to 1.5 and 2 ml) of the sample showed no carry-over effect. A 0.5-min purge (1 ml),
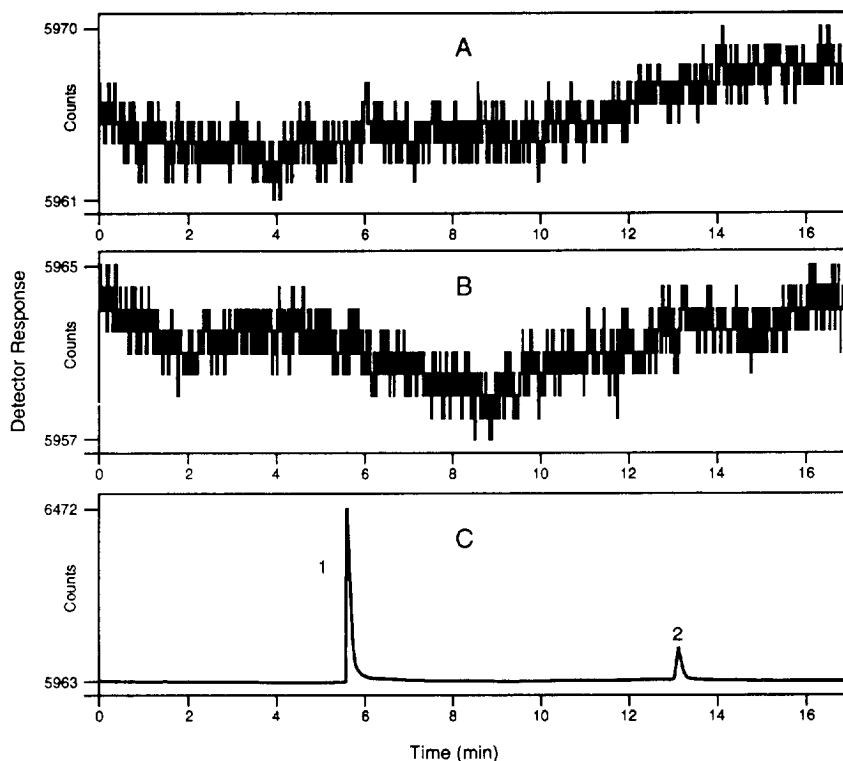

Fig. 3. Carry-over effect. (A) Purge volume 2 ml. (B) purge volume 1.5 ml. (C) purge volume 1 ml. Peaks: 1 = acetonitrile; 2 = chlorobenzene.

however, showed carry-over at a moderate level. A 2-ml wash sample was used for all subsequent studies. Carry-over effect is a matrix-dependent phenomenon related to the volatility and functional groups present. Fig. 4 shows a comparison of chromatograms for n-propylbenzene. Fig. 4A is a chromatogram obtained for a liquid injection of n-propylbenzene. Fig. 4B is a chromatogram obtained for a blank injection from an empty vial directly after the n-propylbenzene injection. Fig. 4C and D are chromatograms for n-propylbenzene and for an acetonitrile sample injected after the n-propylbenzene. There is a minimum carry-over effect (ca. 40 ppm) for this matrix. That effect did not pose any problem for neat liquid injection with percent concentrations. The oven temperature program was 100°C and programmed to 200°C at 6°C/min. The transfer

line and the valve temperature were held at 75 and 95°C, respectively. All other conditions are the same as described in the Experimental section.

The valving system prior to the split injector may be operated at different temperatures. No noticeable peak broadening was observed with the acetonitrile–chlorobenzene test solutions under the conditions described above because the liquid sample from the loop injector was transferred into a regular split injector. This reduced any problem from the loop injector. The valve and transfer line temperature may need to be heated or optimized for certain solutes. Two alcohols, 3-methyl-2-butanol and 4-methyl-2-pentanol, were tested at different valve temperatures for chromatographic performance. Resolution degraded at the low valve temperature for
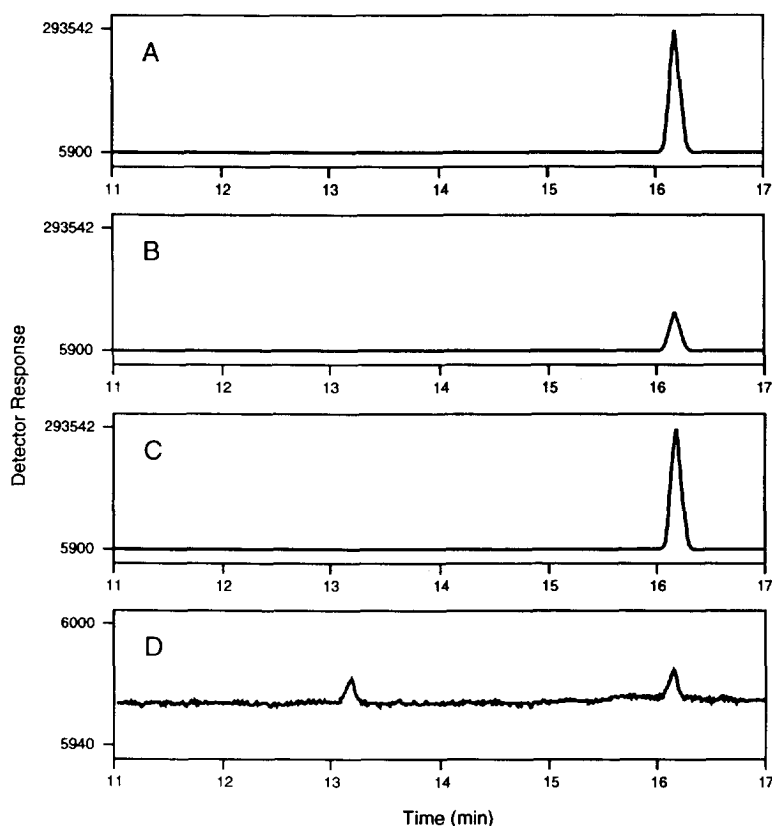

Fig. 4. Carry-over effect. (A) n-Propylbenzene; (B) blank injection, no solvent, no sample; (C) n-propylbenzene; (D) acetonitrile injection, different scale.

several peaks. The high-temperature analysis showed good chromatographic performance. A comparison of the performance of the dual injection system, at a valve temperature of 95°C, with manual liquid injection is shown in Fig. 5 for 3-methyl-2-butanol. No comparison was done using an autosampler because the instrumental setup prevented the use of an autosampler. No significant difference is noticed in the chromato-grams. The peak width of the peak at 5.4 min in the dual injection mode was 3.48 s. The peak width of the corresponding peak in the manual injection was 3.42 s. Other matrices injected, such as N,N-dimethylformamide and N,N-di-methylacetamide, also gave good chromato-graphic performance with the dual injector.

A reproducibility study of the dual injection system was performed for the liquid sample injection using 15% (v/v) chlorobenzene in ace-tonitrile. The relative precision at the 95% confidence level (2.78 s) using absolute area

counts was determined to be 2.9 and 2.6%, respectively. The modifications on the sampling system did not affect the vapor injections. The system gave good results for both vapor and liquid injections. More than 200 injections were performed by the system without any mechanical failure.

3.2. Evaluation using a standard VLE study

A standard test system of a binary mixture of cyclohexane–n-heptane was chosen based on the availability of the components in high purity and the availability of high-quality VLE data from the literature and from data previously collected using a Hewlett-Packard headspace analyzer. This mixture is one of the standards chosen by Fractionation Research, Inc. for evaluation of distillation tray efficiency. Fig. 6 presents repre-sentative chromatograms of the liquid and vapor samples. Fig. 7 illustrates the calibration curves
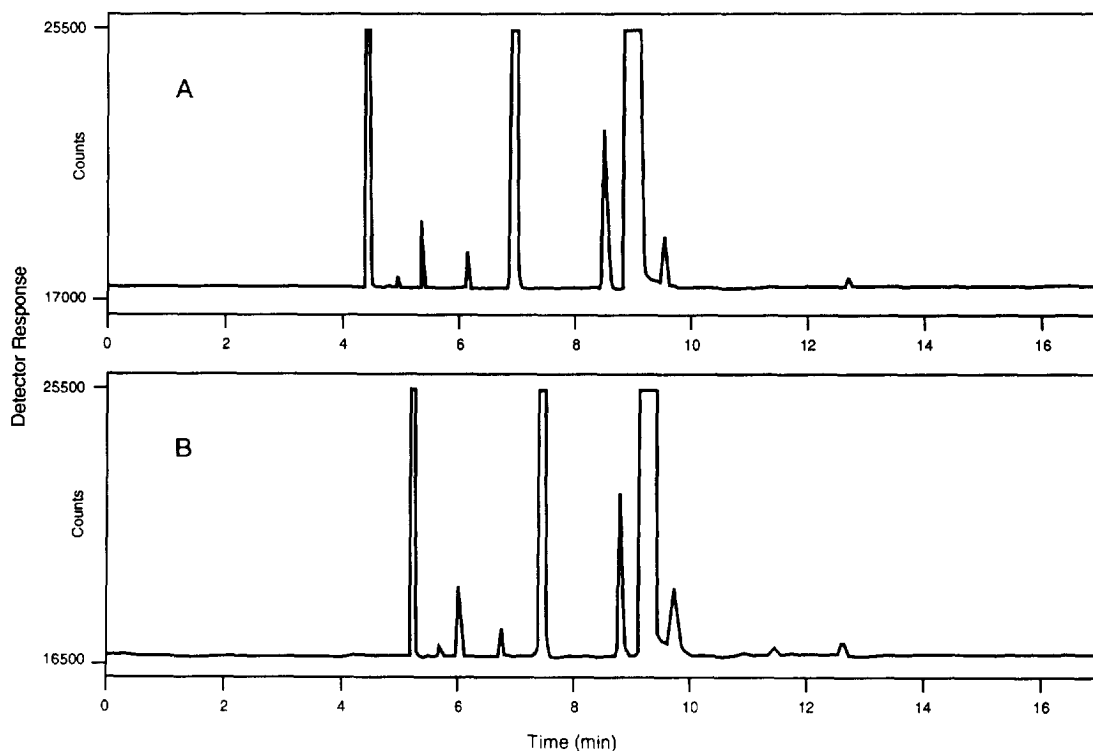

Fig. 5. Comparison for liquid injection of 3-methyl-2-butanol. (A) Manual injection, (B) dual-needle injection.
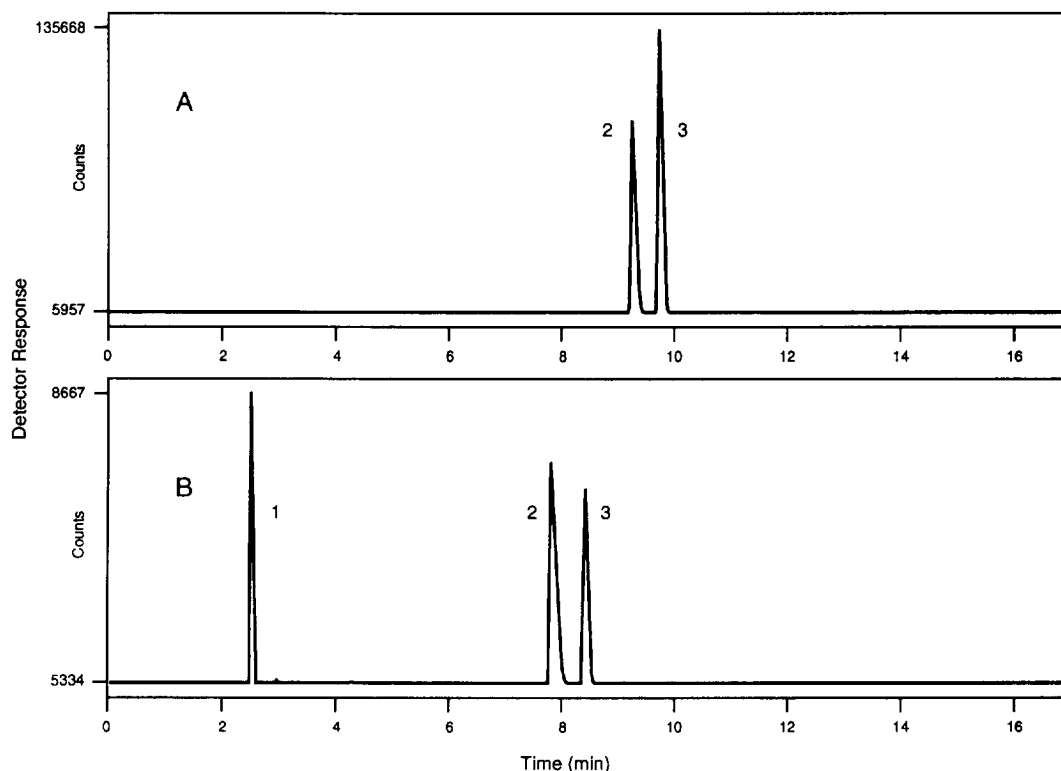
Fig. 6. Liquid and vapor injection of cylcohexane–heptane mixture. (A) Liquid injection, FID; (B) vapor injection, TCD. Peaks: 1 = air; 2 = cyclohexane; 3 = n-heptane.

for cyclohexane and n-heptane. The calibration curves show a good fit with the data over the sample concentration range. The relative volatility results are reported in Table 2. The experimental data were regressed using the Scatchard and Wilson [10] model for liquid phase non-idealities. Fig. 8 illustrates the plots of the mass fraction in the liquid versus the mass fraction in the vapor and the mol fraction in the liquid versus the relative volatility for the binary systems. In Fig. 8A, the dashed curve represents the ideal curve using vapor pressure data for the mixture and the solid straight line in Fig. 8B represents the ideal line, which is the ratio of the components vapor pressure. The solid curves in Fig. 8A and B represent a regression of the data using the Scatchard and Wilson model (the solid straight line in Fig. 8A is used to relate the

actual data to positive and negative deviations from Raoult's Law). In Fig. 8A and B the data lie about the ideal line; thus, as expected, the binary mixture is an ideal system. The dual injection system's results were consistent with the experimental data determined earlier using the conventional headspace system.

4. Conclusions

The dual-needle injector was found to give good performance for VLE studies; it reduced the analysis time by more than half because the GC data from the vapor and liquid injections were generated at the same time, and handling hot chemicals was eliminated thus reducing the potential of chemical exposure. The dual-needle
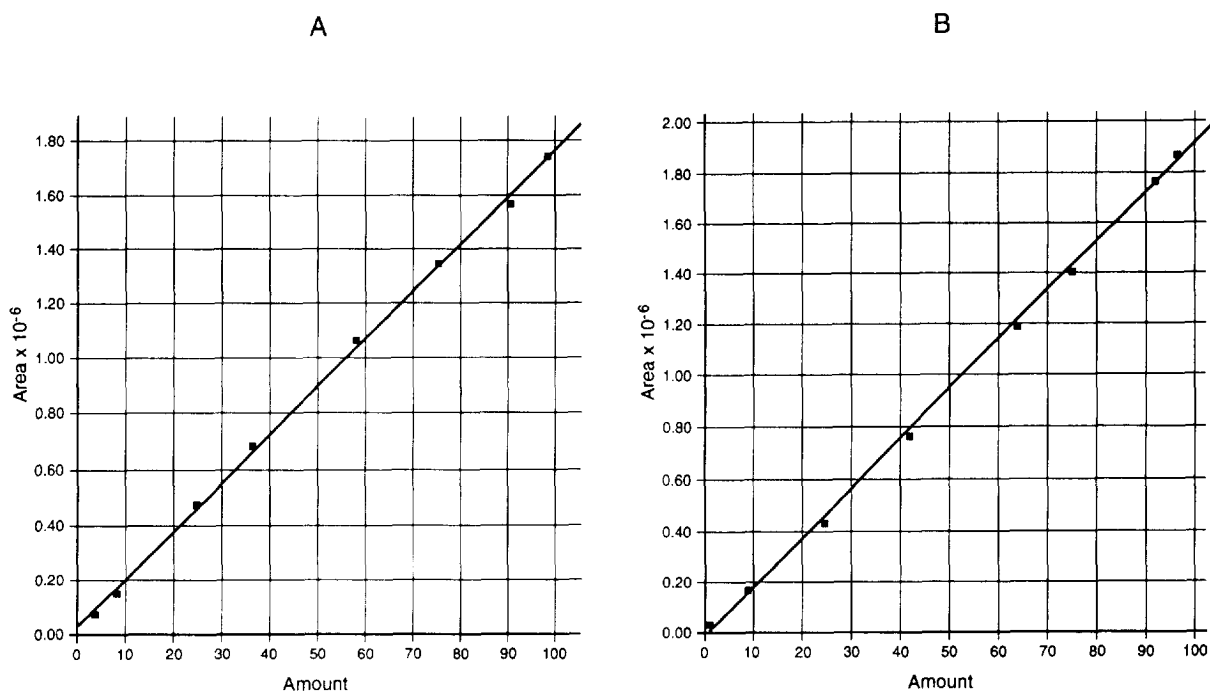
A   B

Fig. 7. Calibration curves for (A) n-heptane and (B) cyclohexane using absolute area counts.

instrument allows collection of representative vapor and liquid samples. Without using this system, liquid samples may be non-representative because of disturbances in the equilibrium, loss of vapor from vial after vapor sampling, and

crystallization or flash evaporation of a component in the syringe. Several other applications were either considered or evaluated, such as liquid–liquid equilibrium studies, high-temperature injections for samples that are insoluble at

Table 2
Relative volatility results for cyclohexane–n-heptane at 75°C

Liquid (%, w/w)		Vapor (%, w/w)		Relative volatility
Cyclohexane	n-Heptane	Cyclohexane	n-Heptane	
1.69	98.31	2.94	97.06	1.76
9.51	90.49	15.03	84.97	1.68
25.10	74.90	37.00	63.00	1.75
42.16	57.84	56.91	43.09	1.81
63.82	36.18	77.12	22.88	1.91
75.19	24.81	85.29	14.71	1.91
92.04	7.96	95.84	4.16	1.99
96.28	3.72	98.18	1.82	2.09

Relative volatility = [% (w/w) vapor$_{cyclohexane}$/% (w/w) vapor$_{n\text{-heptane}}$]/[% (w/w) liquid$_{cyclohexane}$/% (w/w) liquid$_{n\text{-heptane}}$].
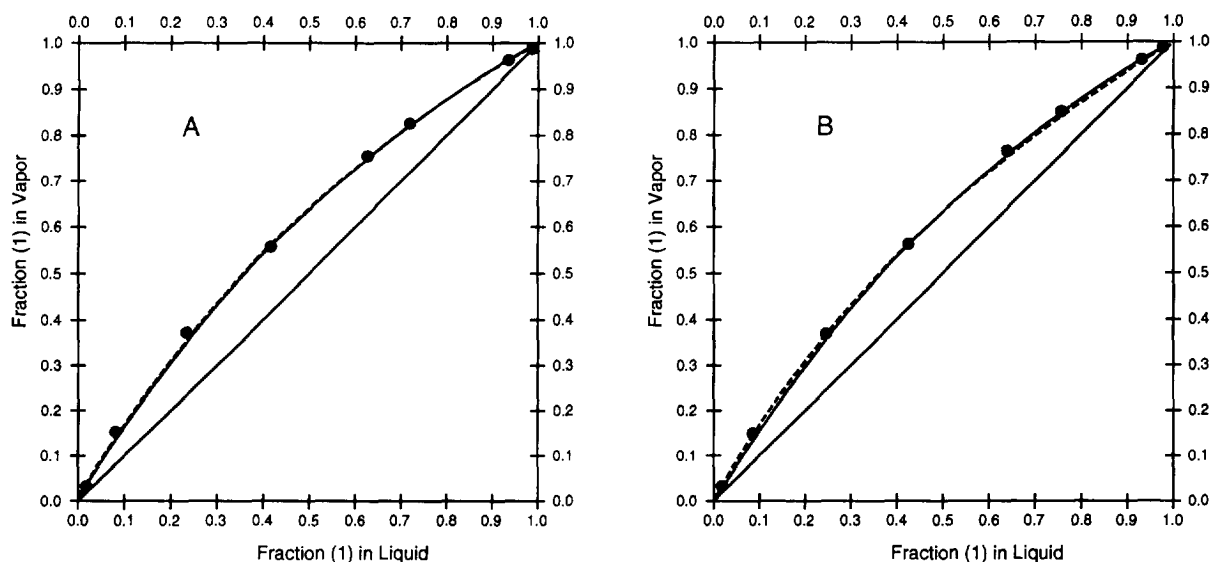
Fig. 8. VLE plots of cyclohexane–n-heptane at 75°C. Components: 1 = cyclohexane, 2 = n-heptane. Broken line, ideal solution at 75°C; solid line, Scatchard and Wilson [10] model at 75°C, V1 = 115.9000, V2 = 157.8700; ● = experimental data, TXY, Obj Fct = A. (A) Conventional, Scatchard and Wilson parameters: U12 = 13.982, U21 = 47.074. (B) Dual injection system, Scatchard and Wilson parameters: U12 = − 126.056, U21 = 143.379. All axes: mass fractions.

room temperature, and implementation on other commercial headspace analyzers.

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