Journal of Chromatography, 112 (1975) 287–295

CHROM. 8469

APPLICATION OF GAS CHROMATOGRAPHIC HEAD-SPACE ANALYSIS FOR THE CHARACTERIZATION OF NON-IDEAL SOLUTIONS BY SCANNING THE TOTAL CONCENTRATION RANGE

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SUMMARY

Head-space analysis by gas chromatography has not only been shown to be useful for analytical purposes, but also to provide a valuable means of obtaining thermodynamically relevant data for solvent–solute characterization. This application was demonstrated for two solute–solvent systems that show positive and negative deviations from Raoult's law, from which activity coefficients at various concentrations and related functions, such as partial and total molar energies of mixing and related excess functions, can be derived.

INTRODUCTION

From the beginning of gas chromatography (GC)[1,2] its possible use for the determination of thermodynamically reliable data, such as partition and activity coefficients and other related functions, for the characterization of solute–solvent interactions was realized. These measurements are based on the precise determination of specific retention volumes using columns in which the liquid phase serves as the solvent that is to be determined. Obviously the results are mainly of interest for understanding the retention behaviour of solutes in GC columns and have not been as useful for the general characterization of technically interesting solvents, as these investigations are restricted to systems of volatile solutes in low volatile solvents.

A more universal method for the same purpose, however, is the technique of GC head-space sampling, provided that serious instrumental problems can be overcome, as discussed below.

The solution to be investigated by head-space analysis is placed in a glass bottle, the temperature of which, after closure of the bottle with a pressure-tight rubber septum, is maintained thermostattically until equilibrium of the volatile components between gas and liquid phases has been established. An aliquot of the gas above the sample is withdrawn either with a gas syringe or with a similar device and transferred to a gas chromatograph, where the volatile components in the gas sample can be separated and quantitated in the usual way. The sample container thus serves in the same manner as a single theoretical plate of a GC column with a liquid stationary phase. Thus head-space analysis opens the possibility of studying such gas–liquid

equilibria without the restriction of the above-mentioned GC method. Apparently it is not necessary to prepare a column with thousands of theoretical plates for each solvent if a single plate is sufficient to study the equilibration of a compound between the two phases.

In a review of head-space analysis with special emphasis on its quantitative aspects, Kolb[3] stressed that the basic relationship of any quantitative head-space analysis is the proportionality of the resulting peak area (A_i') of a compound i to its partial vapour pressure (p_i') above the solution, according to the following equation:

$$A_i' = p_i' C_1 \tag{1}$$

where C_1 = calibration factor. The concentration of the compound in the solution can be calculated according to Henry's law (eqn. 2) because the partial vapour pressure (p_i') of a compound i is related to its vapour pressure (p_i^0) at a given temperature (T) and its concentration in the solution (x_i), corrected for any deviation from ideality by the activity coefficient (γ_i):

$$p_i' = x_i \gamma_i p_i^0 \tag{2}$$

The combined eqns. 1 and 2 are the basis of any quantitative head-space analysis, formulated as eqn. 3:

$$x_i = A_i'/C_1 \gamma_i p_i^0 = A_i'/C_2 \tag{3}$$

where C_1 and C_2 are calibration factors.

The concentration, x_i, of a compound in a given solution can thus be determined if the product $C_1 \gamma_i p_i^0$ is determined by calibration, resulting in the combined calibration factor C_2. Calibration therefore has to be carried out with the pure compound i itself, owing to the specific properties of the vapour pressure at the prevailing temperature and in the same matrix due to the activity coefficient, which represents the interaction between solute and solvent and thus the matrix effects, and furthermore under the same instrumental conditions, as the calibration factor C_1 represents a specific apparatus factor. Moreover, the activity coefficient must be constant to be included in the combined calibration factor C_2, and consequently any quantitative head-space analysis can be carried out in dilute solutions only when a constant activity coefficient can be assumed. These basic relationships for quantitative head-space analysis, its limitations and consequences for various types of samples, including liquids and solids, have been discussed extensively[3,4] and have been summarized by Vitenberg *et al.*[5].

If, however, the concentration of a compound is known, it would appear to be feasible to use the deviation from ideality for determining activity coefficients, even for concentrated solutions, and to follow its dependence on concentration. As the activity coefficient has a dominant position in nearly all thermodynamic calculations, a convenient method for its determination appears to be of utmost importance. Head-space analysis could be the method of choice for this purpose, despite the fact that only a few examples of other than analytical applications have been published up to now.

Rohrschneider[6] measured the partition coefficients of six reference compounds

with different polarities in 80 solvents and correlated these data with solvent polarities, solubility parameters and the molecular volumes of the solvents in order to obtain information on the aromatic selectivity of extraction solvents and solubility data for polymers in diverse solvents. These measurements were performed on a relative basis, a certain solution system with a known partition coefficient being used for reference purposes.

Hachenberg and Schmidt[7] used the head-space method to determine the selective influence of an additional third compound on the separation of two compounds by extractive distillation. Using the same automated instrument as that described below, they reported that in order to obtain the same result 30 working days would have been necessary with classical methods, while with the head-space technique 1 day or even 1 night was sufficient because the instrument operates automatically.

In this paper it is shown how the head-space technique can be used in order to establish vapour pressure diagrams and to calculate activity coefficients and related thermodynamic mixing functions.

INSTRUMENTATION

The main reason why the head-space technique has found only limited application is that there are serious drawbacks to the instrumentation. If a gas-tight syringe is used for transfer of the sample from the thermostatted sample container, condensation may occur, particularly when the concentration of the compounds in the gas phase is high, while losses by adsorption on the walls are possible if the concentration is low[8]. Intrinsic memory effects of gas syringes are known and make every quantitative result suspect.

A second source of problems is the sorption affinity of the rubber septum that must be used for closing the sample bottle, different solubilities being found, depending on the type of rubber septum used and on the polarity of the compounds[6].

The first type of problem has been overcome by replacing the gas-tight syringe with a special electropneumatic dosing system[9], which is now available as an accessory with a universal gas chromatograph (F-42, Bodenseewerk Perkin-Elmer, Überlingen, G.F.R.), whereas previously it was an integral part of a special head-space gas chromatograph (F-40, Bodenseewerk Perkin-Elmer).

This electropneumatic dosing system operates according to the principle shown in Fig. 1. Before the separating column (C) is a T-shaped line leading to the dosing needle (N), which is normally sealed from the atmosphere with a movable cylinder (Z). For dosing, a turn-table containing the sample bottles lifts upwards; the sample bottle (B) shifts the cylinder upwards, and the needle pierces both the rubber septum of the cylinder and that of the sample bottle and penetrates into the bottle. This provides a connection to the carrier gas, and the bottle is filled with carrier gas until the pressure inside it is the same as that in the column (position II). For injection, a solenoid valve (V) cuts off the carrier gas supply. As there is then merely a connection between the sample bottle and the column, the gas in the bottle expands by flowing along to the column, and thus a certain amount of the sample head-space is flushed into the column (position III). The dosing process is completed when the solenoid valve re-opens the carrier gas line. The temperature of the whole system is controlled thermostattically so as to prevent condensation and adsorption. The actual sample

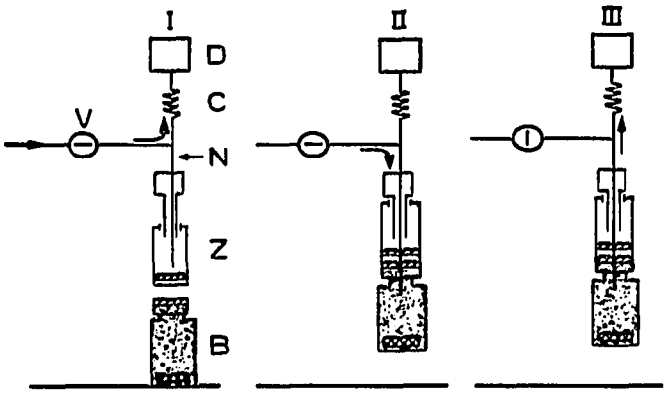


Fig. 1. Principle of head-space sampling with the Multifract F-42 gas chromatograph. D = detector; C = column; N = dosing needle; Z = movable cylinder; B = sample bottle; V = solenoid valve. I = Normal position; II = pressure build-up; III = dosing.

volume is usually not known, but can be calibrated if necessary. It depends on the free gas volume of the bottle, the pressure, the flow resistance of the column and time. It can be varied by varying the time of dosing, which is controlled with a programmer, which also controls the cyclic sequence of all necessary steps during the automated analysis of the 30 samples that fit into the turn-table. Provided that no further problems from the sorption affinity of the rubber septums are involved, this dosing system has been found to reproduce the peak heights within a relative standard deviation of 0.5%, measured on an aqueous calibration mixture for blood alcohol analysis[3,9].

If such good reproducibility cannot be obtained in other instances and with other compounds, it is mostly the septum of the bottles that causes problems. After trying nearly all commercially available septums, a silicon septum, faced with a 0.001-in. PTFE layer (now available from Bodenseewerk Perkin-Elmer) proved to be both sufficiently tight and inert.

Another possible source of errors that should be carefully checked is the limit of the linearity of GC detectors. Particularly if concentrated solutions are analyzed at temperatures at which the compounds may have a high vapour pressure, the amount of sample injected may be beyond the linear range of the detector. It is then convenient to use an outlet splitter between the end of the column and the detector in order to reduce the absolute amount of sample. Sometimes it is advantageous to use a magnetic stirrer, so as to obtain a homogeneous gas mixture in the sample bottles and to prevent the formation of a concentration gradient.

PRINCIPLE OF METHOD

A set of test mixtures with varying compositions are prepared for each solute–solvent system by weighing both components of the binary mixtures. Amounts of 5 ml are transferred with a pipette from each of the test mixtures into the sample bottles (volume *ca.* 25 ml) for head-space analysis. While the absolute amount of the sample is unimportant, its reproducibility influences the precision of the result, as the

remaining free gas volume in the bottle, together with other parameters, determines the volume of gas injected and must therefore be constant.

The bottles are then kept for about 1 h on the turn-table, which is maintained thermostattically at the temperature at which the phase equilibrium is to be investigated. Considerably shorter times are usually sufficient for equilibration, but must be checked. After this equilibration time, the automated analysis cycle is started and all of the sample bottles are analyzed consecutively, while a computer (or integrator) measures the peak areas, which are the final result for these purposes. It is very important at this stage to calculate a response factor for one of the components of these binary mixtures, while the other is used as the reference component. As the peak areas are plotted against mole fractions, this response factor must be expressed and calculated as a molar response factor. For this purpose, the test mixtures can be used and an aliquot is injected directly into the column with a microsyringe in the usual way for GC analysis. The special F-42 instrument that was used in these investigations has a normal injection port for this purpose located parallel to the head-space sampling device. As the composition of the injected sample is known and the resulting peak areas are measured, the molar response factor can be calculated easily. Units for the peak areas in the figures have already been corrected in this way and can therefore be related directly to the vapour pressures.

If corrected peak areas are substituted for the vapour pressures, eqn. 2 becomes

$$A_i' = x_i \gamma_i A_i^0 \tag{4}$$

where A_i' = peak area of component i in the mixture and A_i^0 = peak area of the pure component i. There is, however, a difficulty because x_i is the mole fraction of the component in the solution after equilibration, but from preparing the solution only the total amount of component i is known, and a certain amount has been evaporated into the gas phase during equilibration, thus changing x_i. Owing to the large difference in the molar volumes of a liquid and a gas, this loss of component i in the solution can be neglected, provided that concentrated solutions are involved. The activity of component i and the corresponding activity coefficient are thus calculated according to eqns. 5 and 6:

$$a_i = x_i \gamma_i = A_i'/A_i^0 \tag{5}$$

$$\gamma_i = A_i'/A_i^0 x_i \tag{6}$$

where a_i = activity of component i. If a_i is known, it is possible to calculate the partial free molar energy of mixing by the following equation[10]:

$$\Delta G_i^M = RT \ln a_i = RT \ln (A_i'/A_i^0) \tag{7}$$

and for the total free energy of mixing a binary system from its pure liquid components 1 and 2 by the equation

$$\Delta G^M = RT [x_1 \ln (A_1'/A_1^0) + x_2 \ln (A_2'/A_2^0)] \tag{8}$$

In a similar way, the partial excess free molar energy of mixing can be calculated from the activity coefficient by eqn. 9:

$$\Delta G_i^E = RT \ln \gamma_i \tag{9}$$

and the total excess energy of mixing component 1 and 2 by the equation

$$\Delta G^E = RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \tag{10}$$

Partial and total heats of mixing and entropies of mixing can be derived in a similar way, and any one of these three functions can be calculated when the other two are known[10].

EXPERIMENTAL

The two solute–solvent systems discussed in this paper were investigated under the experimental conditions described below.

Ethanol–n-heptane system

Seven mixtures of ethanol with *n*-heptane of various compositions plus the two pure compounds were investigated at a sample temperature of 70.0°. A Perkin-Elmer Multifract F-40 gas chromatograph with a flame ionization detector was used with a 2 m × 1/8 in. stainless-steel column packed with 15% polypropylene glycol on Celite, 60–80 mesh. The temperature of the column was 65° with nitrogen as carrier gas at the flow-rate of 30 ml/min. The dosing time was 1 sec and the splitting ratio after the column was 1:10.

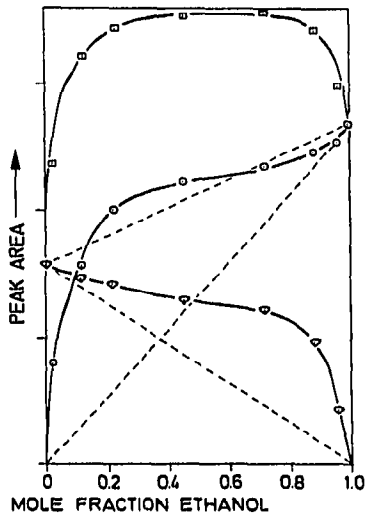
Chloroform–acetone system

Nine mixtures of chloroform with acetone of various compositions plus the pure compounds were investigated at a sample temperature of 36.5°. The compositions of these mixtures are given in Table I and are designated by "a". A Perkin-Elmer Multifract F-42 gas chromatograph with a hot-wire detector was used with a 2 m × 1/8 in. stainless-steel column packed with 10% Carbowax 1540 on Chromosorb R, 60–80 mesh. The temperature of the column was 80° with helium as carrier gas at the flow-rate of 25 ml/min. The dosing time was 3 sec. The quantitative evaluation was carried out with a Perkin-Elmer PEP-II GC data system.

RESULTS

Two solute–solvent systems were selected, one showing positive and the other negative deviations from Raoult's law. Fig. 2 shows the vapour pressure diagram of the system ethanol–*n*-heptane at 70° and Fig. 3 the system chloroform–acetone at 36.5°. These diagrams are obtained if the peak areas resulting from head-space analysis are plotted against the mole fraction of each component, instead of vapour pressure.

The latter system was selected because thermodynamically it is a classical system, for which the necessary constants and the related thermodynamic functions are available, and the results obtained were compared with published data[10,11].



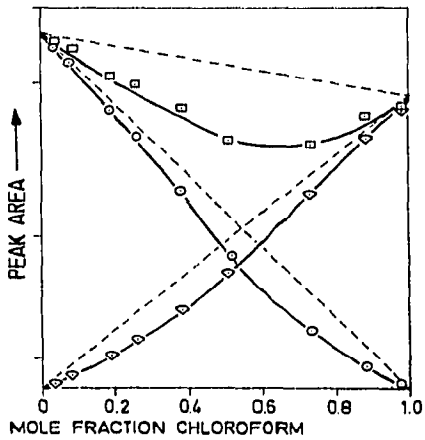


Fig. 2. Partial and total pressure relationships of ethanol–*n*-heptane solutions. Pressures expressed in arbitrary units for corresponding peak areas from head-space chromatogram. ⊙, Ethanol; ▽, *n*-heptane; ⊡, total. Broken lines indicate the relationship had the system been ideal.

Fig. 3. Partial and total pressure relationships of chloroform–acetone solutions. Pressures expressed in arbitrary units for corresponding peak areas from head-space chromatogram. ⊙, Acetone; ▽, chloroform; ⊡, total.

Table I gives a comparison between the experimental activity coefficients measured by head-space analysis and published data[11]. Satisfactory agreement between the two sets of values was obtained.

Finally, it might be instructive to derive the related partial and total free energy of mixing according to eqns. 7 and 8 and the related excess functions from the activity coefficients according to eqns. 9 and 10. These functions are shown in Figs. 4 and 5. It should be mentioned that except for temperature and concentration, no values were used other than the resulting peak areas from head-space analysis.

DISCUSSION

It has been shown that head-space analysis by GC can be used under certain instrumental conditions for characterizing solute–solvent systems by determining activity coefficients and related thermodynamic functions. Compared with the classical GC procedure, in which the solvent to be characterized has to be used as a liquid stationary phase in a specially prepared GC column, the head-space method offers the following advantages:

(1) The head-space method is not restricted to solvents of low volatility. Any solvent can be used without any limitations.

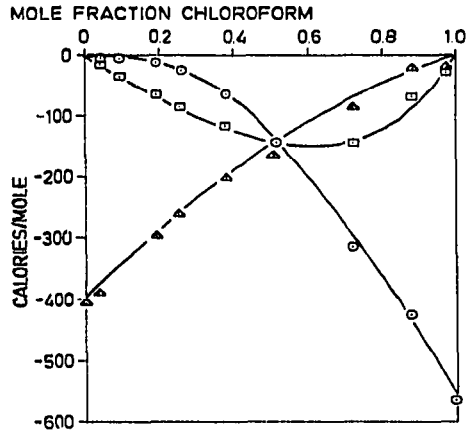
(2) The head-space method is not restricted to dilute solutions, as is the classical GC method; its application covers the whole concentration range from ideal dilute solutions up to the pure compounds themselves. This wide range is covered by the wide linear range of the GC detectors.

TABLE I

COMPARISON OF EXPERIMENTAL AND PUBLISHED ACTIVITY COEFFICIENTS IN CHLOROFORM–ACETONE

Mole fraction of chloroform	*γ (acetone)*	*γ (chloroform)**	
0.00	1.00	—	a,b
0.037	1.00	0.52	a
0.060	0.99	0.51	b
0.088	1.00	0.53	a
0.184	0.98	0.59	b
0.188	0.98	0.62	a
0.257	0.96	0.66	a
0.263	0.95	0.65	b
0.361	0.91	0.69	b
0.384	0.90	0.72	a
0.424	0.88	0.72	b
0.508	0.82	0.77	b
0.515	0.79	0.77	a
0.581	0.75	0.82	b
0.662	0.68	0.88	b
0.732	0.60	0.87	a
0.802	0.56	0.95	b
0.877	0.50	0.97	a
0.918	0.46	0.99	b
0.975	0.40	0.97	a
1.000	—	1.00	a,b

* a = Values calculated from head-space analysis at 36.5°; b = published values[11].



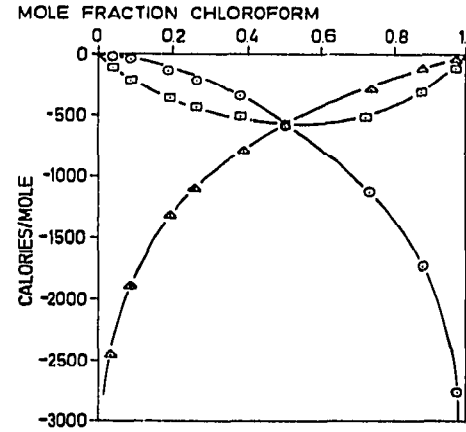


Fig. 4. Partial and total free energies of mixing for chloroform–acetone solutions. △, Chloroform; ⊙, acetone; ⊡, total.

Fig. 5. Partial and total excess free energies for chloroform–acetone solutions. Symbols as in Fig. 4.

(3) The head-space method is based on peak area determinations, which can be carried out with the same degree of precision and accuracy as retention time measurements.

(4) Consecutive analyses on a series of sample bottles can easily be automated, while preparing a special column for each solvent cannot.

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