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A novel methodology for the identification of azeotropic binary mixtures by TG-FTIR techniques

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Abstract

A methodology based on simultaneous thermogravimetric and infrared spectrometric (TG-FTIR) analysis was developed, providing data on the evaporation temperatures of a liquid mixture and on the presence of azeotropic points. The technique also enables the estimation of the azeotropic composition and the attainment of preliminary data on the thermal stability of the components. The method may be applied to the investigation of any binary system where the separation of the contributions of each component to the recorded IR spectra is possible. Although the dynamic configuration of the TG-FTIR experiments causes the method to be less accurate than conventional techniques, its main advantage is the very limited amount of sample required for experimental runs (<30 μl per run). The methodology proved to be potentially useful for a preliminary investigation of the possibility of separation by distillation methods of binary homogeneous mixtures. The much lower quantities of samples required make the TG-FTIR technique attractive due to the significant reduction of time, costs and of safety and disposal problems associated to conventional methods. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thermogravimetric analysis; Infrared spectrometric analysis; Azeotrope; Vapour–liquid equilibria; Distillation

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1. Introduction

The separation of a homogeneous liquid mixture into its individual components to recover products, by-products, and raw unreacted materials is an important step in many industrial processes. Among the various methods that might be used for effecting the separation, distillation is the most important one that is used commercially. In particular, it remains the method of choice for the large scale separation of non ideal mixtures [1].

Knowledge of the vapour–liquid equilibria (VLE) and azeotropic points is essential for the synthesis and design of a distillation process. In addition, the rapid development of chemical and pharmaceutical industry, leads to new and improved reaction schemes and thus to the production of new chemicals and new mixtures of known chemicals. Therefore, there will be a continuous need for new phase equilibrium and azeotrope data.

Phase equilibrium and azeotropic data can be obtained either experimentally or by thermodynamic modelling using equations of state or equations for

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Nomenclature

A	absorbance
c	concentration (mol/l)
D	integral of I with respect to time (cm^{-1} s)
F	volumetric gas flow rate (l/s)
I	integrated absorbance (cm^{-1})
K	experimental constant relating I to concentration (cm^{-1} mol^{-1})
l	optical path length (cm)
n	total amount of compound evolved (mol)
t	time (s)
Y	molar fraction
ϵ	extinction coefficient (cm^{-1} mol^{-1})
$\tilde{\nu}$	wavenumber (cm^{-1})

excess Gibbs energy. Numerous VLE data have been published both in scientific journals and in the form of data collections [2–6]. Useful data on azeotropic compositions are available for individual systems in several publications [7], and as collections in a few books [8,9]. In some of the various data collections, coefficients necessary for thermodynamic modelling are also presented [2,6]. Predictive methods have become increasingly valuable due to the fact that experimental data may be missing or available only for limited ranges of temperatures, pressures or compositions [10,11]. However, it is recognised that experimental data should be used whenever possible as VLE cannot yet be always reliably predicted [12].

Many apparatus have been developed for the accurate measurement of the VLE and azeotropic composition. Several reviews on experimental procedures and equipment have been published in the literature. Despite the numerous variants, the equipment can be classified into two basic categories [13–15], e.g. static equipment [4,16] and dynamic equipment [17–22]. The principle of equilibrium determination consists of evaporating a mixture and allowing phase equilibrium to become established at a certain pressure, whereupon the temperature and compositions of the content of the still pot and of the vapour in equilibrium are determined by using suitable analytical techniques. It is also possible to carry out the determination isothermally, the pressure that is established at a constant temperature being measured.

Azeotropes are usually determined during VLE measurements. Both homogeneous and heterogeneous temperature minimum azeotropes at moderate pressure can also be determined directly and with good accuracy with the help of a suited micro spinning band column [7].

Despite the continuous technical evolution, the apparatus most widely used to measure liquid–vapour equilibria operate with mixture quantities ranging from 50 to 500 ml. A few millilitres of mixture are necessary if a micro spinning band is used for azeotrope determination. Composition analysis of the samples is performed with common analytical techniques, such as gas chromatography and refractive indices measurement, that require preliminary calibration and are likely to be very time-consuming.

Therefore, the aim of the present study is to verify if a methodology based on simultaneous thermogravimetric and infrared spectrometric (TG-FTIR) analysis could be advantageously applied to the attainment of preliminary data on the evaporation temperatures, the presence of azeotropic points and the estimation of azeotropic compositions of a liquid binary homogeneous mixture. Although the dynamic configuration of the experiments will inevitably cause the method to be less accurate than conventional techniques, the methodology could be a useful tool for preliminary investigations and screening exercises, since it presents several advantages. For example, a very limited amount of sample is required for experimental runs (<30 μl per run) which means reduction in costs, safety and disposal problems. Moreover, the procedure uses an internal calibration method which allows a considerable reduction in time. FTIR analysis of vapour phase permits on line monitoring of the evolved vapour compositions with time. This possibility is very attractive as FTIR analysis may not only be used to obtain quantitative information on the azeotropic composition of a mixture but may also allow the identification of impurities or decomposition products formed in significant quantities during the vaporisation runs thus providing evidence of thermal stability of the system.

To gain insight into the potentialities of this novel methodology, several vaporisation measurements involving binary homogeneous systems were carried out. In particular, systems with different VLE characteristics were considered, i.e. A zeotropic system and several temperature minimum and temperature maximum azeotropic systems.

2. Experimental

2.1. Materials

The methodology developed was validated by experimental tests at ambient pressure on the binary systems listed in Table 1. The compositions of the binary mixtures used in experimental runs are listed in Table 2. The binary solutions were obtained starting from bidistilled water and the following commercial substances and mixtures which were used as supplied: benzene purchased from Baker; acetic acid glacial of RPE grade, cyclohexane of RPE grade, *N*,*N*-dimethylformamide (DMF) of HPLC grade and 1,4-dioxane of RPE grade purchased from Carlo Erba; hydrobromic acid solutions 48 and 63 wt.% and tetrachloromethane of HPLC grade purchased from Aldrich.

2.2. Techniques

Simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) data were obtained using a Netzsch STA 409/C thermoanalyser. Runs were carried out using a 100% nitrogen purge gas flow of 80 ml/min (at 25 °C and 1 atm) at heating rates between 1 and 10 °C/min. Samples were positioned in alumina crucibles with a total volume of 70 μl and an internal diameter of 5 mm. A lid with a 1mm diameter hole was used to cover the crucible, as shown in Fig. 1.

Table 2
Composition of binary mixtures used in experimental runs

System	Mixture	HVC (mol%)
Water/DMF	a	74.7
	b	85.0
	c	89.6
	d	96.8
HBr/water	a	27.5
	b	6.5
	c	5.9
	d	3.9
Dioxane/water	a	35.4
	b	51.2
	c	62.4
	d	82.1
CCl_4/acetic acid	a	93.9
	b	98.0
	c	98.8
Benzene/cyclohexane	a	23.1
	b	41.6
	c	51.5
	d	56.3
	e	65.8
	f	90.3

TG-FTIR simultaneous measurements for the on-line analysis of vapours formed during TG runs were carried out coupling a Bruker Equinox 55 FTIR spectrometer to the Netzsch TG using a 4 mm internal diameter and 800 mm long Teflon tube. Both the transfer line and the head of the TG balance were heated at a constant temperature of 180 °C to avoid condensation phenomena. FTIR measurements were carried out with a MCT detector in a specifically

Table 1
Normal boiling points of the individual components and azeotropic data at ambient pressure for the binary mixtures considered in the present work

HVC[a]	LVC[b]	Boiling point HVC (°C)	Boiling point LVC (°C)	Azeotropic data	
				HVC (mol%)	bp (°C)
Water	DMF	100.0	153.0	Zeotropic	
Hydrogen bromide	Water	−66.5	100.0	16.6	125
Water	1,4-Dioxane	100.0	101.3	51.7	87.8
Tetrachloromethane	Acetic acid	76.8	118.1	96.2	76.0
Benzene	Cyclohexane	80.1	80.8	53.8	77.6

[a] HVC: higher volatility compound.

[b] LVC: lower volatility compound.

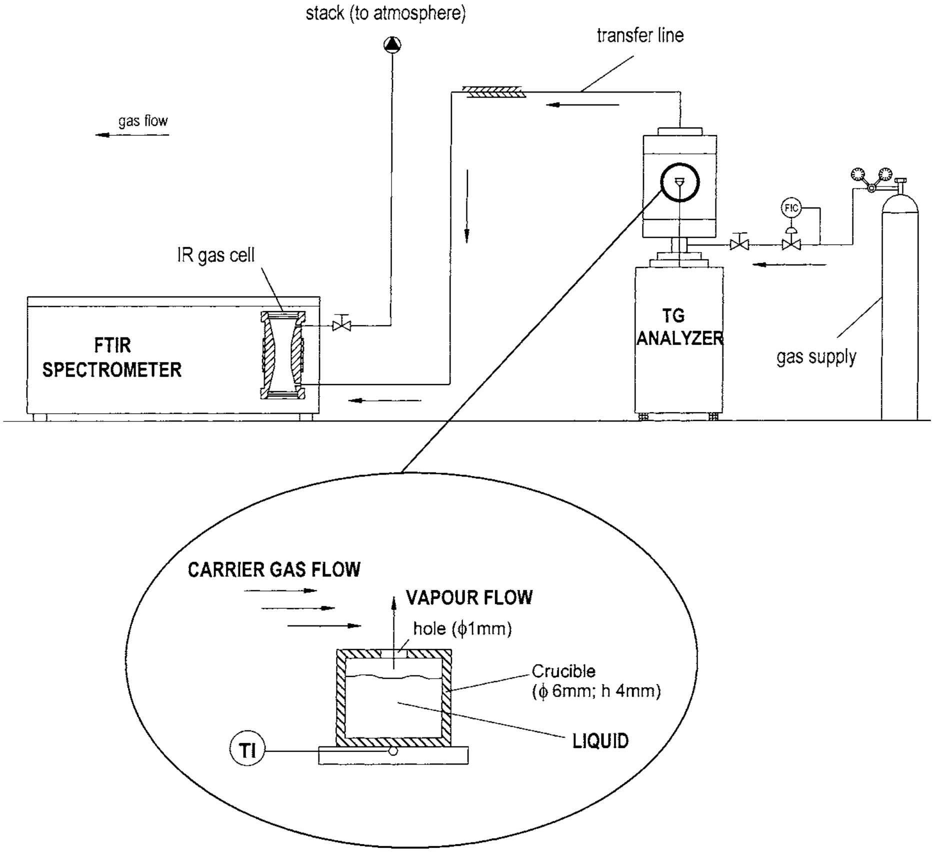

Fig. 1. TG-FTIR coupling system (TI: thermocouple).

developed low volume gas cell (8.7 ml) with a 123 mm path length, heated at a constant temperature of 200 °C. A scheme of the TG-FTIR coupling is given in Fig. 1.

A residence time of 50 s in the transfer line could be evaluated for the evolved gases. This value was assumed as the time delay correction to be used for the comparison of TG and FTIR results. During TG-FTIR runs, spectra were collected at 4 cm^{-1} resolution, co-adding 16 scans per spectrum. This resulted in a temporal resolution of 9.5 s.

2.3. Measurement of vapour composition during TG-FTIR runs

A linear relation between spectral absorbance at a given wavenumber and concentration of a gaseous compound is postulated by the Lambert–Beer law. However, due to the limited resolution of FTIR measurements, the Lambert–Beer relation is generally used in an integral form on a characteristic wavenumber interval.

$$I = \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} A(\tilde{\nu})\,\mathrm{d}\tilde{\nu} = \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \varepsilon(\tilde{\nu}) lc\,\mathrm{d}\tilde{\nu} = Kc \qquad (1)$$

where I is the integral value, A the measured absorbance, ε the extinction coefficient of the gaseous compound, l the optical path length used in the measurement, c the concentration and $(\tilde{\nu}_1, \tilde{\nu}_2)$ the wavenumber interval selected for the measurement; K is a constant that should be independent of concentration if deviations from the Lambert–Beer law may be neglected, as in the case. The value of K depends on the compound considered, the wavenumber interval, the temperature of the gas, the optical path length and the instrument resolution. Thus, the constant K should be obtained by a calibration procedure for all the compounds of interest.

TG-FTIR measurements may thus be used to generate a specific gas profile to monitor qualitatively the evolution of a gas as function of time or of the temperature of the TG furnace. This requires the availability of a wavenumber absorption interval of the compound of interest free of additional contributions from other substances, unless deconvolution methods are used [23,24]. The following wavenumber intervals were selected for the substances considered in the present study: 1836–1724 cm^{-1} acetic acid; 722–624 cm^{-1} benzene; 2988–2812 cm^{-1} cyclohexane; 3017–2717 cm^{-1} DMF; 3006–2800 cm^{-1} dioxane; 2480–2462 cm^{-1} hydrogen bromide; 820–726 cm^{-1} tetrachloromethane; 4025–3792 cm^{-1} water.

The gas profiles generated by Eq. (1) may be used to estimate the vapour composition. The FTIR software allows the integration of Eq. (1) with respect to time.

$$D = \int_{t_1}^{t_2} \left[\int_{\tilde{\nu}_1}^{\tilde{\nu}_2} A(\tilde{\nu})\, \mathrm{d}\tilde{\nu} \right] \mathrm{d}t = K \int_{t_1}^{t_2} c\, \mathrm{d}t \tag{2}$$

where the (t_1, t_2) interval is the time interval of interest. The total molar amount n of the compound of interest evolved during the interval (t_1, t_2) may be expressed as follows:

$$n = \int_{t_1}^{t_2} Fc\, \mathrm{d}t \tag{3}$$

where F is the total volumetric gas flow rate at the actual gas temperature in the measurement cell.

If the total volumetric gas flow rate through the FTIR measurement cell is constant, the value of integral (2), D, is easily related to n.

$$n \approx F \int_{t_1}^{t_2} c\, \mathrm{d}t = \frac{F}{K} D \tag{4}$$

Since during TG-FTIR runs a constant purge gas flow rate of 80 ml/min (at 25 °C and 1 atm) is used, Eq. (4) is valid if the volumetric contribution of the vapours generated during the TG run to the total volumetric flow rate may be neglected with respect to the purge gas flow, as in the case.

Thus, if the linear relation between concentration and absorbance on a specific wavenumber interval given by Eq. (1) may be assumed in the range of concentrations of interest, the FTIR absorption measurements may be used to estimate the composition of vapours formed during TG runs on any time interval. Since a binary mixture, constituted of components A and B, is vaporised in the experiments, the mean molar fraction Y_A of vapour A with respect to total vapour formed in the time interval (t_1, t_2) of interest may be expressed as

$$Y_A = \frac{n_A}{n_A + n_B} = \frac{K_B D_A}{K_B D_A + K_A D_B} \tag{5}$$

where n_A are the moles of vapour A evolved in the time interval of interest given by Eq. (4), n_B the moles of vapour B and K_A, K_B, D_A and D_B are defined in Eqs. (1) and (2).

The values of K_A and K_B may be estimated using an internal calibration method. The value of D_A on the time interval $(0, t_f)$ corresponding to the entire run duration may be obtained from the experimental data using Eq. (2). The value of n_A in Eq. (4) calculated on the same time interval is the total quantity of component A initially present in the sample, since the complete vaporisation of the sample takes place during the TG-FTIR runs. Thus, the value of K_A may be easily estimated by Eq. (4) and K_B may be obtained by the same method.

Therefore, Eq. (5) allows evaluating the vapour composition over any time interval (t_1, t_2). The minimum time interval Δt that can be used in Eq. (2) is obviously the interval between the acquisition of two following IR spectra. Thus, the composition of vapour phase at time intervals of 9.5 s may be estimated from the analysis of experimental FTIR data.

2.4. Procedures

TG-FTIR runs were performed on liquid mixtures of known initial composition, prepared as described earlier. Samples of about 10–30 μl (equivalent to 15–30 mg for the mixtures considered in the present work) were positioned in the alumina crucible at the beginning of the run using a chromatographic syringe. Runs were performed using heating rates comprised between 1 and 10 °C/min, starting at 30 °C. The temperature at the end of the run was always sufficiently high to perform the complete vaporisation of the sample during the experimental run.

3. Results and discussion

3.1. Zeotropic mixtures

Water/DMF is a well-known zeotropic binary system. Water/DMF liquid mixtures have a complete solubility over the entire composition range. As shown in Table 1, water is the higher volatility compound (HVC) of the system, and DMF is the lower volatility compound (LVC).

The results of a constant heating rate TG-FTIR run on 26 μl (25.71 mg) of a 3.2 mol% DMF solution in water are reported in Fig. 2. Fig. 2(a) shows the sample weight loss and the temperature as a function of time, and Fig. 2(b) shows the corresponding weight loss rate of the sample. The temperature increase in TG-FTIR runs results in a constant increase of the sample weight loss rate, until complete vaporisation is achieved. In all the runs performed in this study, the weight loss and the weight loss rate curves had the qualitative shape shown in Fig. 2. Fig. 2(c) shows the qualitative concentration profiles of the components of the vapour evolved from the sample, obtained evaluating integral I (Eq. (1)) as a function of time for the two components. The profiles were obtained from the analysis of FTIR data following the procedure discussed in Section 2. The Fig. 2 points out that the concentration of water in the vapour reaches a maximum at about 1120 s (corresponding to a temperature of about 105 °C) and constantly decreases at higher temperatures. On the other hand, the presence of DMF in the vapour is not detected until 850 s (corresponding to a temperature of about 80 °C). At higher temperatures, the concentration of DMF in the vapour increases constantly as temperature is increased, until the complete vaporisation of the sample. Thus, the results show that, as expected, the vapour formed during the sample vaporisation progressively enriches in the LVC of the mixture.

The presence of a maximum in the vapour concentration of water (the HVC) is due to the temperature increase, that causes an increase in the evaporation rate of the component until the bubble point of the residual liquid binary mixture is approached. Data in Fig. 2 clearly point out that the concentrations of water and DMF in the vapour constantly increase up to 1120 s (105 °C) only as a consequence of the temperature increase and of increasing equilibrium partial pressures of water and DMF vapours in the crucible.

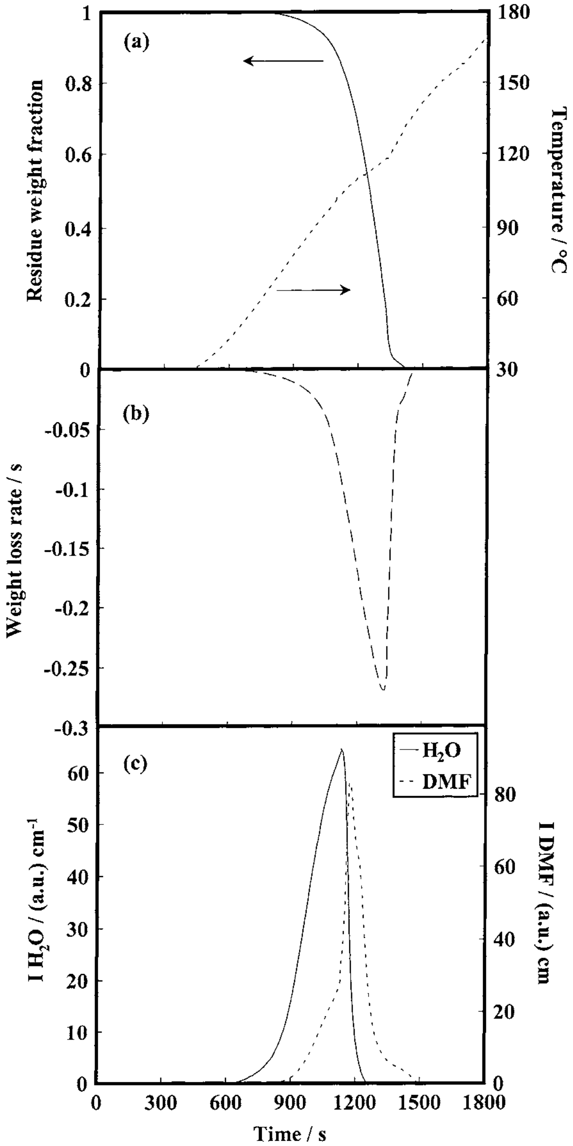

Fig. 2. TG-FTIR data recorded during the vaporisation of a 3.2 mol% DMF solution in water (5 °C/min): (a) weight loss and temperature; (b) weight loss rate; (c) integrated absorbance (I).

A qualitative representation of the behaviour of vapour and liquid composition is given in Fig. 3(a). In the figure, segment 1 represents the trend of the liquid composition while the temperature is lower than the bubble point of the mixture. At temperatures below the bubble point of the mixture, molecular diffusion through the hole in the crucible lid causes the vapours to enter the nitrogen flow and to be carried through the

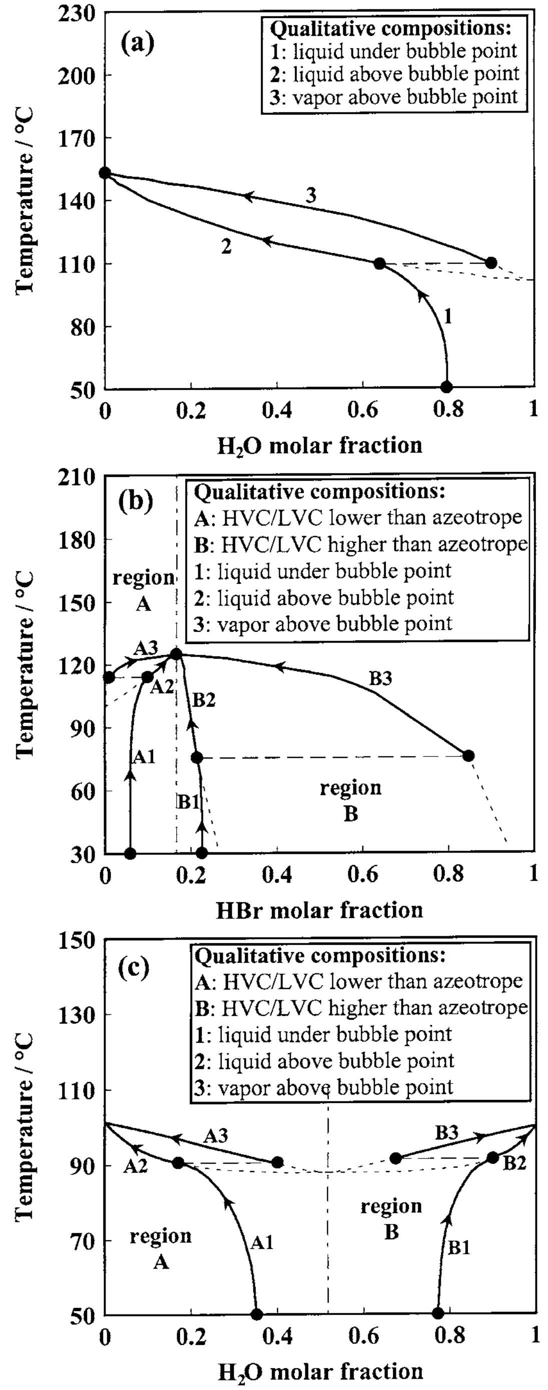

Fig. 3. Qualitative behaviour of liquid and vapour composition during the vaporisation of (a) water/DMF mixtures (zeotropic system), (b) HBr/water mixtures (maximum temperature azeotrope) and (c) water/dioxane mixtures (minimum temperature azeotrope).

FTIR sampling cell (Fig. 1). Segments 2 and 3 represent the qualitative trends of the liquid and the vapour compositions respectively after the mixture temperature reaches the bubble point. Obviously, due to the dynamic configuration of the run, the actual vapour and liquid compositions will only approximate the equilibrium compositions represented by segments 2 and 3. As a matter of fact, above the bubble point of the mixture a pressure gradient is responsible of vapour flow into the nitrogen stream. A rough estimation of the pressure drop through the hole in crucible lid showed that an overpressure of less than 1 Pa is sufficient to generate the vapour flow. This suggests that the data obtained may be considered almost at atmospheric pressure, and that limited deviations from the equilibrium may arise from this factor.

Runs performed vaporising liquid mixtures at different water:DMF ratios showed the same qualitative behaviour.

3.2. Binary mixtures with a temperature maximum azeotrope

Important differences were observed performing experimental runs on hydrobromic acid solutions. As shown in Table 1, hydrogen bromide (HBr)/water is a binary system that presents complete solubility and was chosen as representative of binary homogeneous systems having a temperature maximum azeotrope [25]. Fig. 4 reports the measured value of the integrated absorbance (*I*) during TG-FTIR runs performed on two hydrobromic acid solutions. Fig. 4(a) shows the results obtained in the vaporisation of 13.5 μl (23.56 mg) of a sample having a HVC:LVC (HBr/water) ratio higher than the azeotropic one (mixture 'a' in Table 2). Fig. 4(b) shows the corresponding results obtained for the vaporisation of 12.5 μl (14.51 mg) of a sample having a HVC:LVC ratio lower than the azeotropic one (mixture 'c' in Table 2). In Fig. 4(a) the concentration profile of the LVC (water) shows the same qualitative behaviour of the LVC in Fig. 2: a constant increase until the complete vaporisation of the sample is achieved. On the contrary, an important difference is present in the concentration profile of the HVC (HBr) with respect to zeotropic systems. As in Fig. 2, the concentration constantly increases up to a maximum at 550 s, and decreases at higher temperatures. However, at a time

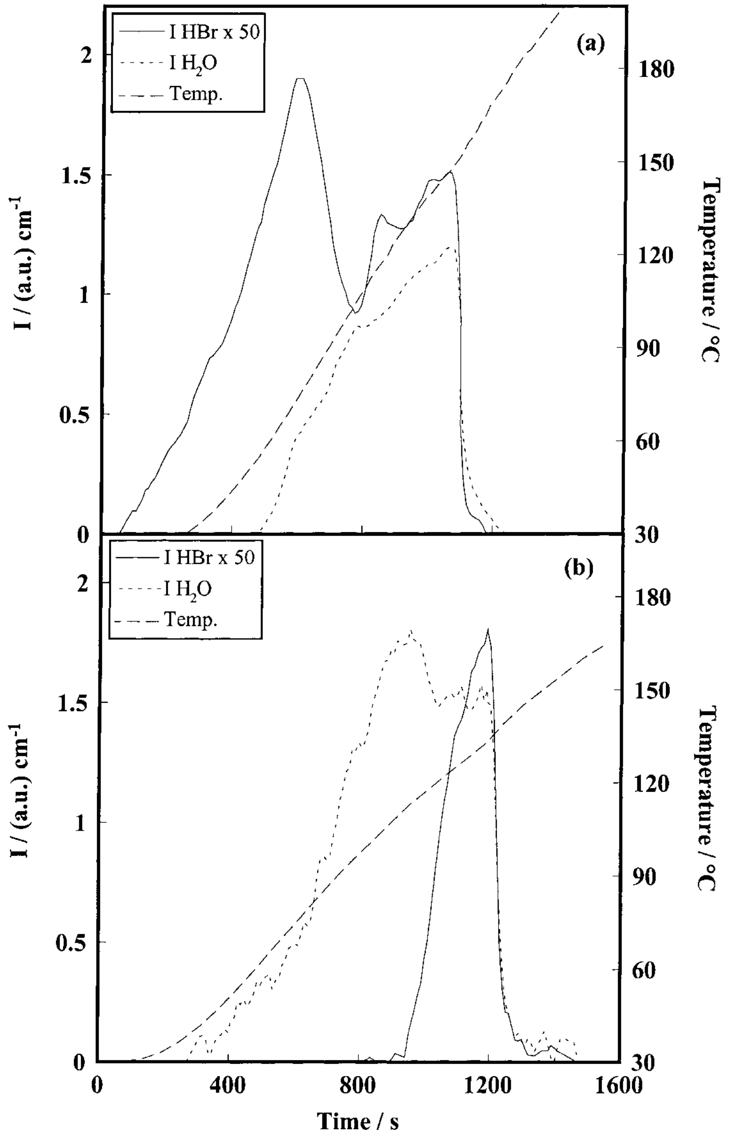

Fig. 4. Integrated absorbance (I) with respect to time during the vaporisation of hydrobromic acid solutions: (a) 27.5 mol% hydrobromic acid, 10 °C/min; (b) 5.9 mol% hydrobromic acid, 5 °C/min.

value of 780 s (corresponding to a temperature of about 110 °C), the concentration profile of HBr has a minimum and at higher temperatures HBr concentration shows a slight increase. Moreover, the ratio between the arbitrary concentration values of water and HBr in Fig. 4(a) seems to be almost constant over the time interval between 820 and 1000 s. The qualitative behaviour shown in Fig. 4(a) was typical of all the hydrobromic acid solutions having a HVC:LVC ratio initially higher than that of the azeotropic mixture.

Fig. 4(b) shows an inverted behaviour of water and hydrogen bromide absorbance profiles with respect to Fig. 4(a). Thus, in the vaporisation of a mixture with a HVC:LVC ratio initially lower than the azeotropic one, water vapour is observed at lower temperatures with respect to hydrogen bromide, even if water is the LVC of the mixture. The qualitative behaviour shown in Fig. 4(b) was typical of all the hydrobromic acid solutions having a HVC:LVC ratio initially lower than that of the azeotropic mixture.

These results may be explained considering the VLE plot for the HBr/water system, reported in Fig. 3(b). All mixtures having a HVC:LVC ratio higher than the azeotropic one fall in region B of the diagram. As shown in the figure, at the beginning of the experimental run, mixtures in region B rapidly reach the bubble point temperature (segment B1). Then, as in runs with water/DMF zeotropic mixtures, the sample mixture evaporates yielding a vapour mainly composed of the HVC (HBr), as shown by segment B3. However, the evaporation causes the liquid composition to enrich in the LVC (water), thus approaching the azeotropic composition (segment B2). When the liquid mixture reaches the azeotropic composition, further evaporation yields a vapour of constant composition, corresponding to that of the azeotropic mixture. Thus, the minimum in the HBr concentration profile and the constant HBr:water ratio shown in Fig. 4(a) may be explained.

On the other hand, mixtures having a HVC:LVC ratio lower than the azeotropic one fall in region A of the diagram. Thus, as shown by segment A1, at the beginning of the run the sample mixture evaporates yielding a vapour mainly composed of water even if this is the less volatile component of the binary mixture. Water evaporation causes the liquid composition to enrich in the more volatile component (HBr), thus approaching azeotropic composition (segments A1 and A2). When the liquid mixture reaches the azeotropic composition, further evaporation yields a vapour of constant composition, corresponding to that of the azeotropic mixture. Thus, the initial evaporation of water, the shape of the water vapour concentration profile and the constant HBr:water ratio found at temperatures higher than 110 °C in Fig. 4(b) may be explained. Nevertheless, it must be recalled that due to the dynamic configuration of the run, the actual vapour and liquid composition will only approximate the equilibrium compositions represented by segments A2, A3, B2 and B3.

3.3. Binary mixtures with a temperature minimum azeotrope

Also systems having a temperature minimum azeotrope showed a specific behaviour in TG-FTIR vaporisation runs. Water/dioxane is a binary system that presents complete solubility and a temperature minimum azeotrope (Table 1). The typical behaviour of integrated absorbance (*I*) during TG-FTIR runs performed on water/dioxane mixtures is reported in Fig. 5. Fig. 5(a) shows the results of a run on 29 μl (29.61 mg) of mixture having a HVC:LVC molar ratio lower than that of the azeotropic one (mixture 'a' in Table 2). The data confirm that, as expected, the presence of the HVC (water) is first detected in the vapour. Water vapour concentration has a maximum at about 1250 s (95 °C), and decreases at higher temperatures. On the other hand, the vapour concentration of the LVC (dioxane) increases until the complete vaporisation of the sample is achieved. All the runs performed vaporising water/dioxane mixtures with HVC:LVC ratios lower than the azeotropic composition showed the same qualitative behaviour.

When water/dioxane mixtures with HVC:LVC molar ratios higher than the azeotropic composition were vaporised, a different behaviour was experienced. The results of a constant heating rate (3 °C/min) TG-FTIR run on 28.5 μl (29.13 mg) of a 82.1 mol% water solution in dioxane are reported in Fig. 5(b). Vaporising this mixture, a maximum in the concentration of the LVC was recorded at about 1300 s. Water was not detected in the vapour until a time value of 750 s (corresponding to a temperature of about 65 °C). At higher temperatures, water vapour concentration steadily increases until the complete vaporisation of the sample. In the final stages of sample vaporisation, the vapour evolved resulted almost only composed by H_2O, even if this is the HVC of the mixture. All mixtures with a HVC:LVC ratio higher than the azeotropic one showed this qualitative behaviour.

A qualitative explanation of these results may be given observing Fig. 3(c). In the case of a mixture with a HVC:LVC molar ratio lower than the azeotropic, as the sample temperature in composition region A approaches the bubble point (segment A1), the equilibrium vapour is more rich in the HVC with respect to the liquid. Thus, the HVC in the liquid evaporates, and the liquid and vapour composition progressively enriches in the LVC (segments A2 and A3 respectively). In the final stages of sample vaporisation, both the liquid and the vapour are composed almost only by the LVC.

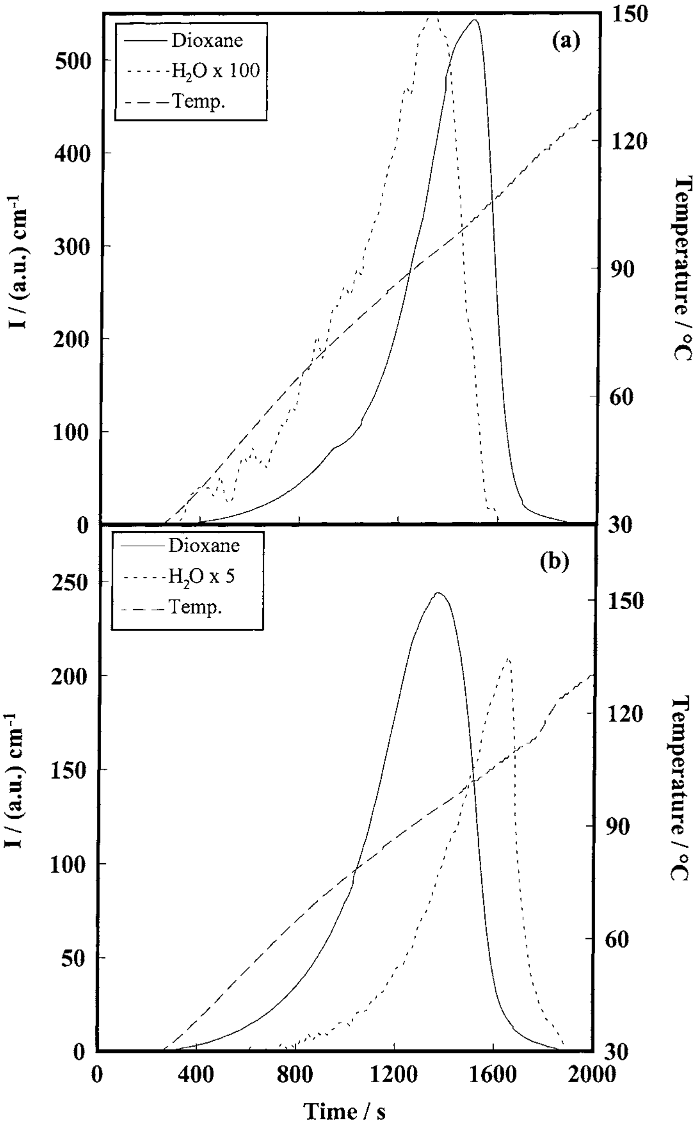

Fig. 5. Integrated absorbance (I) with respect to time during the vaporisation of water/dioxane mixtures: (a) 35.4 mol% water, 3 °C/min; (b) 82.1 mol% water, 3 °C/min.

On the other hand, in the case of a mixture with a HVC:LVC ratio higher than the azeotropic, at the beginning of the run (segment B1) the sample mixture evaporates yielding a vapour mainly composed of dioxane (although dioxane is the LVC of the binary mixture), due to the presence of the minimum temperature azeotrope. Sample vaporisation thus causes the liquid composition to progressively enrich in the HVC (segments B2 and B3). In the final stages of sample vaporisation, both the liquid and the vapour are composed almost only by the HVC (water).

3.4. Qualitative identification of the presence of binary azeotropes

The results reported above point out that TG-FTIR runs on binary homogeneous mixtures may be used as a simple and rapid technique for the preliminary identification of the presence of azeotropes in the composition range of interest. The presence of temperature maximum or temperature minimum azeotropic points may be readily evidenced performing a limited number of experimental runs.

In the case of a temperature maximum azeotrope, as shown in Fig. 3(b), the vapour composition will approach the azeotropic value, independently of the initial composition of the mixture. Moreover, as shown in Fig. 4(b), the vapour at the beginning of the run may be mainly composed by the LVC if the composition of the mixture shows a HVC:LVC ratio lower than the azeotropic one, and the vapour composition will progressively enrich in the HVC as the azeotropic composition of the liquid is approached. Such a behaviour will never be shown by a zeotropic mixture. Thus, the presence of a temperature maximum azeotrope may be readily identified by the following elements: (i) vapour phase approaches a constant composition independently of the initial composition of the liquid mixture; and (ii) vapour will progressively enrich in the HVC if the initial composition of the liquid mixture has a HVC:LVC ratio lower than the azeotropic one.

The presence of a temperature minimum azeotrope in the composition range of interest may be easily detected vaporising a sample of the liquid mixture with the maximum HVC:LVC ratio. If a temperature minimum azeotrope with a HVC:LVC ratio lower than that of the mixture is present, as shown in Fig. 5(b), during the vaporization the vapour composition will progressively enrich in the HVC. This behaviour is not compatible with that of a zeotropic mixture. Furthermore, it is also not compatible with that of a mixture with a maximum temperature azeotrope, since, as shown in Fig. 4(a), these mixtures should yield a vapour that progressively enriches in the LVC, if a HVC:LVC ratio higher than the azeotropic one is present in the liquid vaporised.

Thus, the presence of an azeotrope within the composition range of interest may be detected with no more than two experimental runs, each performed with no more than 30 μl of mixture.

3.5. Quantitative data analysis

As discussed in Section 2, the use of an internal calibration method and of Eq. (5) allows the estimation of the evolved vapour composition by FTIR technique. Thus, data in Figs. 4 and 5 may be analysed in order to obtain the composition of the vapour phase with respect to time. This information may be used to obtain quantitative data on the azeotropic composition of the mixture.

Fig. 6(a) reports the results obtained from the analysis of data in Fig. 4, concerning the HBr/water system. The figure clearly shows that, as expected for a binary system showing a temperature maximum azeotrope, the vapour composition achieves a constant value. What is more important is that the value is approximately the same for all the runs considered, and is comprised between 16 and 18 mol% hydrobromic acid, that well corresponds to the azeotropic composition at atmospheric pressure (16.6 mol% hydrobromic acid).

The results obtained from the analysis of data on the water/dioxane system in Fig. 5 are reported in Fig. 6(b). Fig. 6 shows that, as expected for a system presenting a temperature minimum azeotrope (Fig. 3(c)), the vapour composition at the beginning of the evaporation process closely approaches the azeotropic composition and progressively enriches in the LVC or HVC, depending on the initial HVC:LVC ratio with respect to the azeotropic value. However, it is important to observe that, as shown in Fig. 6(b), the azeotropic composition (51.7 mol% water) belongs to the composition interval identified by the initial composition of the vapours formed in the two runs.

Runs performed reducing the interval in the HVC:LVC initial ratios of the liquid mixtures so as to test mixtures with compositions closer to the azeotropic one, allow reducing the uncertainty on the actual value of the azeotropic composition. The results of two further runs performed on the water/dioxane system are reported in Fig. 6(b). One refers to a mixture with initial composition of 62.4 mol% water. As expected, the initial composition of the vapours formed during the run is closer to the azeotropic composition. The other run refers to a mixture with initial composition of 51.2 mol% water. It is noticeable how the composition of the vapours formed keeps close to the azeotropic composition over almost the run time duration. The results are not surprising if we consider that the initial composition of the liquid mixture was very close to the azeotropic one (51.7 mol%).

To study the reliability of the method, further experiments were performed on two non-aqueous

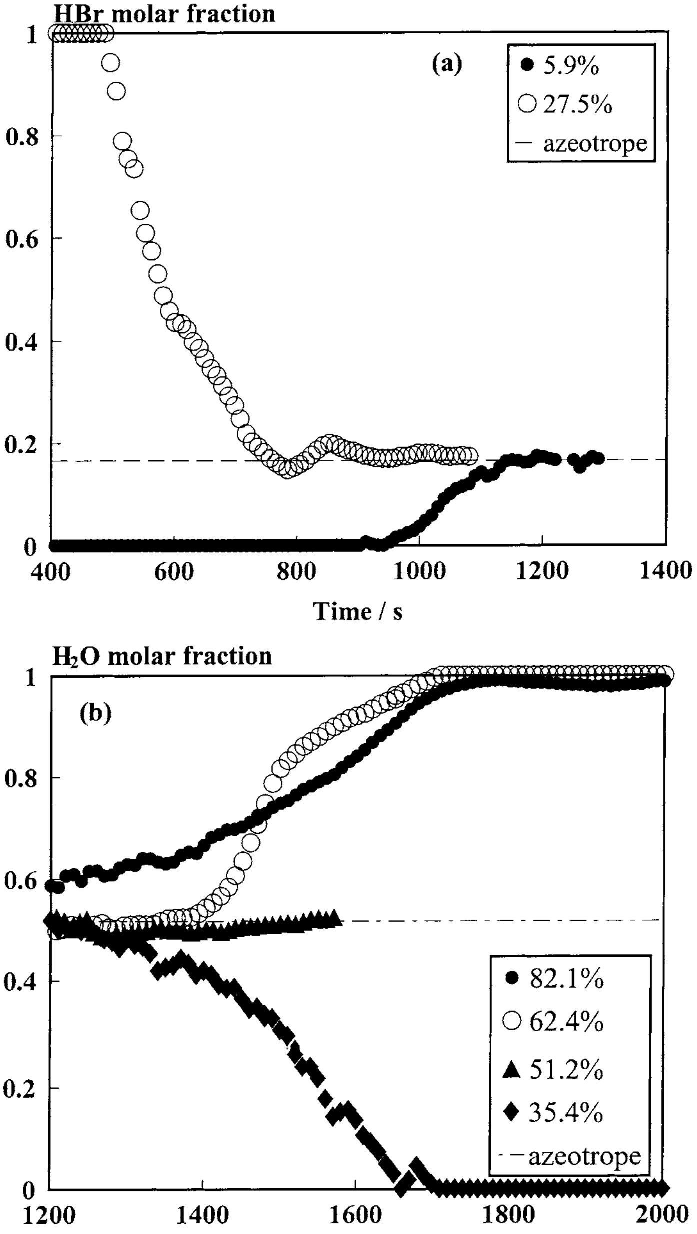

Fig. 6. Composition of the vapour evolved during the vaporisation in TG-FTIR runs of (a) HBr/water mixtures and (b) water/dioxane mixtures.

systems, the tetrachloromethane/acetic acid system and the benzene/cyclohexane system. As shown in Table 1, these systems are rather critical, the first having an azeotropic composition very close to that of a pure component (96.2 mol% tetrachloromethane), and the second showing a very limited temperature difference (<3 °C) between the boiling temperatures of the azeotrope and of the pure components. The

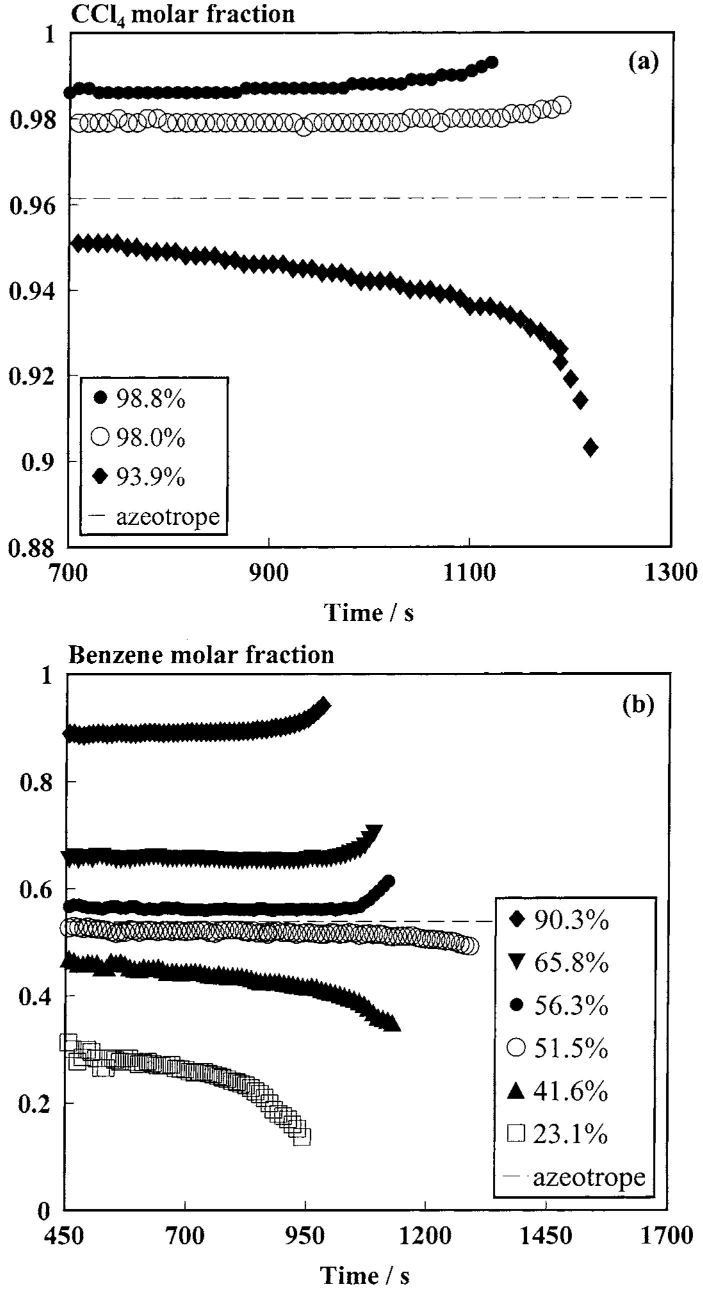

Fig. 7. Composition of the vapour evolved during the vaporisation in TG-FTIR runs of (a) CCl_4/acetic acid and (b) benzene/cyclohexane mixtures.

results reported in Fig. 7 show that also for these systems the method was able to detect the presence of an azeotrope and to estimate the azeotropic composition with a sufficient accuracy (±2%).

3.6. Limitations in the use of the technique

In the earlier sections the capabilities of the TG-FTIR technique were discussed. However, it is also useful to briefly summarise the more important limitations in the use of the technique.

- Vapour composition is measured by IR technique. Thus, the vapour-phase spectra of the two components should have a wavenumber absorption interval reasonably free from the contributions of the other component, or the separation of the contributions to recorded spectra should be possible by deconvolution techniques [23,24].
- TG-FTIR runs in conventional devices can only be performed at atmospheric pressure and starting at temperatures equal or higher than ambient temperature. Therefore, in these devices mixtures with bubble temperatures below ambient temperatures may not be studied, and pressure dependence of azeotropic composition may not be directly explored.
- The liquid sample of a heterogeneous system is characterised by a light phase stratified on a heavy phase. Thus, the methodology can only be reliably applied to homogeneous systems using conventional TG-FTIR devices.
- Configuration of experimental runs is dynamic, and evaporation takes place in an open system. Thus, data may only be an approximation of equilibrium compositions.

4. Conclusions

The method developed, based on the use of TG-FTIR techniques, proved to be able to yield at least preliminary qualitative and quantitative information on the presence of azeotropes in binary homogeneous systems. Although the dynamic configuration of the experiments causes the method to be less accurate than conventional techniques, its main advantage is the very limited amount of sample required for experimental runs (<30 μl per run, corresponding to <50 mg by weight for the mixtures examined in the present work). Moreover, FTIR analysis of vapour phase may also enable the identification of impurities or decomposition products during the vaporisation runs. Thus, the methodology proved to be potentially useful for a preliminary investigation of the possibility of separation by distillation methods of binary mixtures. Having in mind the limitations discussed above, the very low quantities of samples required make the TG-FTIR technique attractive due to the limited time required by the experiments, and the reduction of safety and disposal problems associated to conventional methods.

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