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The use of a separability coefficient for the screening of vapor–liquid enrichment by TG-FTIR analysis

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Abstract

A novel methodology for the screening of vapor–liquid enrichment in binary homogeneous systems is presented. The methodology is based on the estimation of a separability coefficient from experimental data obtained by thermogravimetry with Fourier transform infrared spectrometry (TG-FTIR) of the evolved gases. The technique may be applied to the investigation of any system where the separation of the contributions of each component to the recorded IR spectra is possible. Experimental tests on several binary zeotropic and azeotropic mixtures were carried out at atmospheric pressure and the results were compared to available relative volatility data. The separability coefficient obtained by a batchwise evaporation of binary mixtures in TG-FTIR experiments was shown to reasonably approach the trend of relative volatility. The very limited amount of sample required for experimental runs (less than 30 μl/run) and the use of an internal calibration method make the TG-FTIR technique attractive for the preliminary screening of the separability of binary homogeneous mixtures.

Keywords: Thermogravimetric analysis; Infrared spectrometric analysis; Azeotrope; Vapor–liquid enrichment; Relative volatility; Distillation

1. Introduction

Information on the vapor–liquid enrichment tendency of a liquid mixture is essential for the design and development of separation processes. Traditional measurements that yield reliable quantitative data require specific devices, are very time-consuming and, despite the continuous technical evolution, require generally mixture quantities ranging from 50 to 500 ml [1–3]. The availability of straightforward experimental methodologies allowing the screening of mixtures separability rapidly and using a limited amount of sample would be very attractive.

So far, thermogravimetry with Fourier transform infrared spectrometry (TG-FTIR) of the evolved gases has been mainly used for the investigation of thermal decomposition products of miscellaneous materials. A review of the conventional applications of this technique is given by Materazzi [4]. The technique was recently applied to the identification of azeotropic points in binary mixtures [5]. The possibility of carrying out a sort of batchwise open distillation by

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Nomenclature

A	absorbance
C	concentration (mol l^{-1})
D	integral of I with respect to time (cm^{-1} s)
F	volumetric gas flow rate (l s^{-1})
I	integrated absorbance (cm^{-1})
K	experimental constant relating I to concentration (cm^{-1} mol^{-1} l)
l	optical pathlength (cm)
n_i	amount of ith compound evolved (mol)
$n_{i,\mathrm{L}}$	amount of ith compound in the liquid phase (mol)
$n_{\mathrm{T,L}}$	total moles of the liquid phase (mol)
$n^0_{i,\mathrm{L}}$	initial amount of ith compound in the liquid phase (mol)
t	time (s)
T_f	TG run final temperature (°C)
T_s	TG run initial temperature (°C)
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Greek letters

ε	extinction coefficient (cm^{-1} mol^{-1} l)
$\tilde{\nu}$	wavenumber (cm^{-1})
σ	separability coefficient

Subscripts

i	ith component
j	jth component
m	total number of components

vaporizing mixtures in the thermogravimetric (TG) analyzer and detecting the composition of the vapor formed by on-line quantitative FTIR analysis suggests that the field of application of this technique could be extended to the experimental evaluation of separability of mixtures.

The aim of the present work is to investigate whether a novel methodology based on TG-FTIR analysis can be used to attain preliminary information on the vapor–liquid enrichment of binary homogeneous mixtures and hence on their ease of separation by distillation. Such a methodology would be helpful for the preliminary screening of new mixtures of known chemicals as well as of mixtures of new chemicals. It could be extremely useful and advantageous especially in pharmaceutical or fine chemicals laboratories where the available mixture quantities are usually very limited and analytical instrumentation such as TG and FTIR are commonly employed. The method requires a modest amount of sample (less than 30 μl/run), which results in a considerable reduction in costs, safety and disposal problems. Moreover, by using an internal calibration procedure, experiments require limited time. FTIR analysis of vapor phase allows on-line monitoring of the evolved vapor compositions with respect to time and temperature. This, in turn, permits the achievement of information on mixture separability over a wide interval of compositions available in a single experiment. Moreover, FTIR analysis may also provide evidence of thermal instability of the system since FTIR analysis allows decomposition products that may be formed during the vaporization runs to be identified. In order to illustrate the potentialities of this novel methodology, several measurements involving binary homogeneous zeotropic and azeotropic systems are reported.

2. Experimental

2.1. Materials

Experimental data on the following binary systems were obtained:

- benzene–cyclohexane,
- hydrogen bromide–water,
- hydrogen chloride–water,
- 2-propanol–1,2-dichloroethane,
- water–*N*,*N*-dimethylformamide,
- water–*N*-methyl-2-pyrrolidone,
- water–1,4-dioxane.

The characteristics of these systems are summarized in Table 1. The experimental tests required the characterization of binary mixtures with different composition.

The binary solutions were obtained starting from twice distilled water and the following commercial substances and mixtures which were used as supplied: benzene purchased from Baker; *N*,*N*-dimethylformamide (DMF) of HPLC grade, 1,4-dioxane of RPE grade, 2-propanol of RPE grade, cyclohexane of RPE grade, 1,2-dichloroethane of RPE grade, and aqueous

Table 1
Normal boiling points of the individual components (HVC Higher Volatility Compound, LVC Lower Volatility Compound) and azeotropic data at ambient pressure for the binary mixtures considered in the present work[a]

HVC	LVC	Boiling point of HVC (°C)	Boiling point of LVC (°C)	Azeotropic data		Relative volatility data
				mol% HVC	b.p. (°C)	
Water	DMF	100.0	153.0 (a)	Zeotropic		(b)
Water	NMP	100.0	202.0 (c)	Zeotropic		(c)
Water	1,4-Dioxane	100.0	101.3 (a)	51.7 (d)	87.8 (d)	(e)
2-Propanol	1,2-Dichloroethane	82.4 (a)	83.5 (a)	47.0 (f)	74.1 (f)	(g)
Benzene	Cyclohexane	80.1 (a)	80.8 (a)	53.8 (a)	77.6 (a)	(e)
Hydrogen bromide	Water	−66.5 (a)	100.0	16.6 (h)	125 (h)	(h)
Hydrogen chloride	Water	−85 (a)	100.0	11.1 (i)	108.6 (i)	(i)

[a] From (a) Lide [6]; (b) Hala et al. [7]; (c) *N*-Methyl-2-Pyrrolidone Handbook [8]; (d) Stichlmair and Fair [9]; (e) calculated from the azeotropic data using the Margules equation [9]; (f) measured at 100.32 kPa, from Gmehling and Bölts [10]; (g) calculated using the UNIFAC model [11]; (h) Pascal [12]; (i) Chrétien [13].

hydrochloric acid 37 wt.% purchased from Carlo Erba (Milan); aqueous hydrobromic acid 48 and 63 wt.%, and *N*-methyl-2-pyrrolidone (NMP) of HPLC grade purchased from Aldrich.

Water–DMF, water–NMP, water–1,4-dioxane, 2-propanol–1,2-dichloroethane, and benzene–cyclohexane solutions with different compositions were prepared by mixing weighed quantities of the two compounds, whereas for hydrogen bromide–water and hydrogen chloride–water mixtures, weighed quantities of water and either aqueous hydrobromic acid or hydrochloric acid were mixed.

2.2. *Techniques and procedures*

Measurements were carried out using a Netzsch STA 409/C thermoanalyzer coupled to a Bruker Equinox 55 FTIR spectrometer by a heated transfer line. Further details on the experimental apparatus are given elsewhere [5].

TG runs were carried out using a 100% nitrogen purge gas flow of 80 ml/min (at 25 °C and 1 atm). Samples were positioned in alumina crucibles with a total volume of 70 μl and an internal diameter of 4 mm. A lid with a 1 mm diameter hole was used to cover the crucible. Samples of about 10–30 μl and of known initial composition were positioned in the alumina crucible at the beginning of the run using a chromatographic syringe. Runs were performed using a heating rate comprised between 1 and 10 °C/min, starting at 30 °C up to a final temperature between 90 and 260 °C. The temperature at the end of the run was always sufficiently high to allow the complete vaporization of the sample during the experimental run. Sample composition, temperature range and heating rate of TG-FTIR runs used to obtain the results reported in the following are summarized in Table 2.

The on-line analysis of vapors formed during TG measurements was carried out collecting spectra at 4 cm^{-1} resolution, co-adding 16 scans per spectrum. This resulted in a temporal resolution of 9.5 s.

2.3. *Specific profiles of vaporized compounds*

The typical results of the TG-FTIR runs performed on the liquid mixtures considered in the present work consist in a weight loss curve, that can be reported as a function of time or temperature, and in a sequence of IR spectra recorded every 9.5 s. The IR spectra collected were used to generate specific profiles to monitor the evolution of the vapors as function of time or of the temperature of the TG furnace. This required the availability of a region of the infrared spectrum specific to the compounds of interest and absent of contributions from the other components, unless deconvolution methods are used [14,15]. It must be recalled that the carrier gas (nitrogen) is transparent to IR radiation, and thus does not interfere in the measurements.

For each compound of interest the profiles were calculated using the following expression:

$$I_i = \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} A_i(\tilde{\nu})\,\mathrm{d}\tilde{\nu} \qquad (1)$$

Table 2
Initial sample composition, temperature range and heating rate of TG-FTIR runs used to obtain the results reported in the figures

System	Run	Initial weight (mg)	Approximate volume[a] (μl)	Initial HVC content (mol%)	T_s (°C)	T_f (°C)	Heating rate (°C/min)
Water–DMF	a	25.68	27	74.7	30	170	5
	b	26.35	27	85.0	30	170	10
	c	25.77	26	91.7	30	160	3
Water–NMP	a	22.64	22	93.5	30	260	7
	b	22.21	22	95.8	30	260	7
Water–1,4-dioxane	a	29.61	29	35.4	30	120	3
	b	30.50	30	51.9	30	120	3
	c	28.94	28	62.4	30	120	3
	d	29.13	29	82.1	30	120	3
2-Propanol–1,2-dichloroethane	a	28.32	24	15.1	30	120	5
	b	25.85	24	40.0	30	100	3
	c	23.70	26	74.5	30	120	5
Benzene–cyclohexane	a	21.96	28	23.1	30	90	1
	b	24.32	30	41.6	30	90	1
	c	22.17	27	51.5	30	90	1
	d	21.41	26	56.3	30	90	1
	e	21.02	25	65.8	30	90	1
	f	18.63	22	90.3	30	110	3
Hydrogen bromide–water	a	14.51	13	5.87	30	150	5
	b	18.51	15	5.87	30	150	5
	c	22.35	13	27.5	30	180	10
	d	22.87	13	27.5	30	150	5
Hydrogen chloride–water	a	24.31	23	5.13	30	150	5
	b	26.09	23	16.7	30	150	5

[a] Approximate values based on the chromatographic syringe scale.

where I_i is the integrated value of absorbance for compound i, A_i the measured absorbance at a single wavenumber, and $(\tilde{\nu}_1, \tilde{\nu}_2)$ the range of wavenumbers selected for the measurement. Table 3 shows the infrared regions selected for the compounds of interest.

Table 3
Wavenumber intervals selected for the calculation of the integrated absorbance (I in Eq. (1)) of the compound of interest

Compound	Wavenumber interval (cm^{-1})
Benzene	722–624
Cyclohexane	2988–2812
1,2-Dichloroethane	744–676
DMF	3017–2717
1,4-Dioxane	3006–2800
Hydrogen bromide	2480–2462
Hydrogen chloride	2971–2952
NMP	3022–2748
2-Propanol	3717–3577
Water	4025–3792

3. Results and discussion

3.1. Analysis of experimental data

The raw FTIR data were used to obtain quantitative data on vapor and liquid composition as a function of time and temperature. The data analysis procedure was based on an integral form of the Lambert–Beer's law:

$$I_i = \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \varepsilon_i(\tilde{\nu}) l C_i \, \mathrm{d}\tilde{\nu} = K_i C_i \qquad (2)$$

where I_i is the integrated absorbance of compound i defined in Eq. (1), l the optical pathlength used in the measurement, ε_i and C_i are, respectively, the extinction coefficient and the concentration of compound i in the gas phase. K_i is a constant that should be independent of concentration if deviations from the Lambert–Beer's law may be neglected, as in the case [16]. The value of K_i depends on the compound considered and on several experimental parameters, such as the temperature of the gas, the optical pathlength and the instrument resolution. Thus K_i should be obtained for each compound of interest by a simple calibration procedure.

The integrated absorbance, I_i, may be integrated on a time interval (t_1, t_2) of interest:

$$D_i = \int_{t_1}^{t_2} I_i \,\mathrm{d}t = K_i \int_{t_1}^{t_2} C_i \,\mathrm{d}t \tag{3}$$

The time-integrated signal, D_i, may be easily correlated to the quantity of the compound of interest vaporized during the time interval (t_1, t_2). This may be expressed as:

$$n_i = \int_{t_1}^{t_2} FC_i \,\mathrm{d}t \tag{4}$$

where F is the total volumetric gas flow rate at the actual gas temperature in the measurement cell and n_i the total moles of compound i vaporized during that time interval. If the total volumetric gas flow rate through the FTIR measurement cell is constant, the value of integral (3), D_i, is easily related to n_i as:

$$n_i \approx F \int_{t_1}^{t_2} C_i \,\mathrm{d}t = \frac{F}{K_i} D_i \tag{5}$$

During TG-FTIR runs a constant purge gas flow rate of 80 ml/min (at 25 °C and 1 atm) was used. Eq. (5) is valid if the volumetric contribution of the vapors generated during the TG run to the total volumetric flow rate through the FTIR measurement cell is small.

The constant K_i can be calculated integrating Eq. (5) over the complete duration of the experimental run. In this case, n_i would be equal to the total amount of compound i in the sample used for the experimental run. Thus, the composition of vapor phase at a generic time interval (t_1, t_2) may be easily calculated from Eq. (5) as:

$$y_i = \frac{n_i}{\sum_{j=1}^{m} n_j} = \frac{D_i/K_i}{\sum_{j=1}^{m} D_j/K_j} \tag{6}$$

where y_i is the molar fraction of component i in the vapor formed in the time interval (t_1, t_2), and m the total number of components in the sample ($m = 2$ for a binary mixture).

If the time interval (t_1, t_2) in Eqs. (3)–(5) is chosen as the time between the acquisition of two successive IR spectra (9.5 s for the experimental runs reported in the present study), y_i well represents the vapor molar fraction at time $(t_1+t_2)/2$. This procedure was used to generate the profiles of vapor composition with respect to time in the experimental runs.

On the other hand, if integral (3) is calculated on the elapsed time (0, t), the total quantity of compound i vaporized up to time t may be calculated from Eq. (5). This procedure was applied to calculate the total moles of each compound vaporized up to time t.

The number of moles of component i that are in the liquid at time t and the total moles of the residual liquid were calculated from a simple molar balance:

$$n_{i,\mathrm{L}} = n_{i,\mathrm{L}}^{0} - n_i \tag{7}$$

$$n_{\mathrm{T,L}} = \sum_{i=1}^{\mathrm{m}} n_{i,\mathrm{L}} \tag{8}$$

where $n_{i,\mathrm{L}}$ are the moles of component i in the liquid at time t, $n_{i,\mathrm{L}}^{0}$ the initial amount of moles of component i in the liquid, $n_{\mathrm{T,L}}$ the total moles of liquid and n_i the total moles of compound i vaporized up to time t. Eqs. (7) and (8) were applied to calculate the moles of the different compounds in the liquid as a function of time. Introducing the molecular weights in Eq. (8), the total weight of the liquid at time t could be calculated. Moreover, the composition of the liquid phase at a generic time interval (t_1, t_2) may be easily calculated as follows:

$$x_i = \frac{n_{i,\mathrm{L}}}{\sum_{j=1}^{m} n_{j,\mathrm{L}}} \tag{9}$$

where x_i is the molar fraction of component i in the liquid. Therefore, the molar composition of the liquid phase could be calculated as a function of time.

The mass balances discussed above allow determining a separability coefficient, defined as:

$$\sigma = \frac{y_i/y_j}{x_i/x_j} \tag{10}$$

where i is the more volatile component of the binary mixture. The separability coefficient is coincident with the relative volatility [17] if equilibrium values of liquid and vapor molar fractions are used in Eq. (10). Since the TG-FTIR runs are carried out in an open system, σ may only approach the value of relative volatility. However, it may be used to represent the tendency to vaporize of the more volatile component with respect to the less volatile component as a function of composition and temperature in the experimental runs. The above definition of σ refers to the pure components in the mixture, therefore, in azeotropic systems the separability coefficient, as well as the relative volatility, can have values below unity.

3.2. Composition of liquid and vapor phase during TG-FTIR runs on binary systems

In a previous publication, the capability of estimating the vapor phase composition during the vaporization runs by the FTIR measurements was shown [5]. The mass balances discussed above also allow the calculation of the composition of the residual liquid. An example is given in Fig. 1, where the liquid composition and the composition of vapor formed during the vaporization run are reported for a water–DMF sample. The results were obtained vaporizing 27 μl (25.68 mg) of a sample having initial composition of 74.7 mol% water. Water–DMF is a well-known binary zeotropic system. As shown in Table 1, water is the higher volatility compound (HVC) and DMF is the lower volatility compound (LVC). Fig. 1(a) reports the molar composition of the residual liquid and of the vapor formed as a function of time. The figure shows that initially the vapor is almost only composed by water, the HVC. As the sample is progressively vaporized and the temperature in the thermobalance rises, the vapor enriches in DMF, the LVC, until the vapor results almost only composed by DMF. Correspondingly, the figure shows that the liquid is almost only composed of DMF in the final part of the run, since water is almost completely vaporized at lower temperatures. This behavior is confirmed by the results reported in Fig. 1(b) that shows the cumulative amount of water vaporized as a function of time during the run, calculated from Eq. (5). The overall moles of the residual liquid and of the vapor formed as a function of time are also shown in the figure. The sample was composed of 0.6 mmol water and 0.2 mmol DMF. The figure shows that if the vaporization run had been carried out only up to, e.g. 1120 s, only about 0.4 mmol of water (i.e. the 67% of the water present initially in the liquid sample) and 0.03 mmol of DMF would have been evaporated, while the residual liquid would have been concentrated from 25.3 to 45.8 mol% DMF.

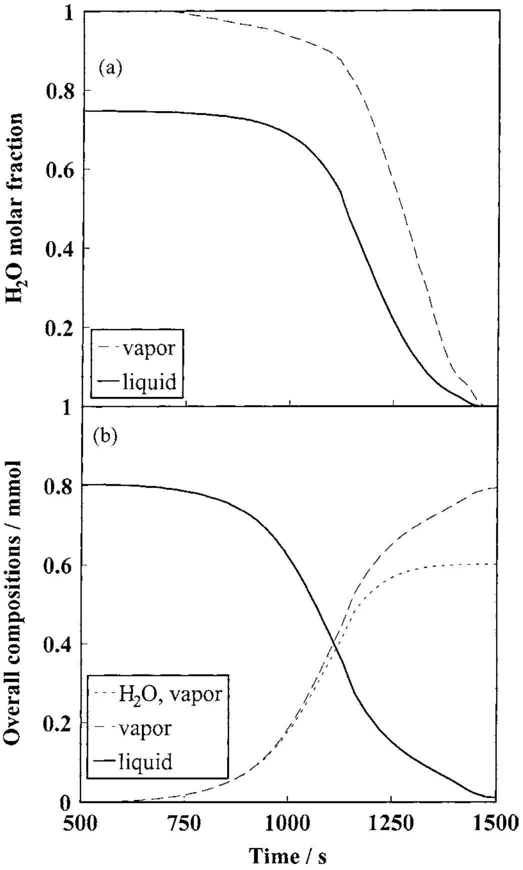

Fig. 1. Molar composition (a) and overall compositions (b) of evolved vapor and of residual liquid as a function of time during the evaporation of a water–DMF solution in the TG-FTIR system (run a in Table 2).

Thus, results as those shown in Fig. 1 may allow a preliminary estimation of the vapor–liquid enrichment that one could expect in a batchwise open distillation mode, provided that the composition values reasonably approach equilibrium. This point will be further discussed in the followings.

Data similar to those shown in Fig. 1 were obtained for each experimental run carried out. Fig. 2 shows the results obtained for runs performed on the water–1,4-dioxane and the water–HCl systems. The former is a binary homogeneous system that presents complete solubility. Water is the HVC of the system and 1,4-dioxane is the LVC (b.p. = 101.3 °C). As shown in Table 1, the system has a temperature minimum azeotrope at 51.7 mol% water with

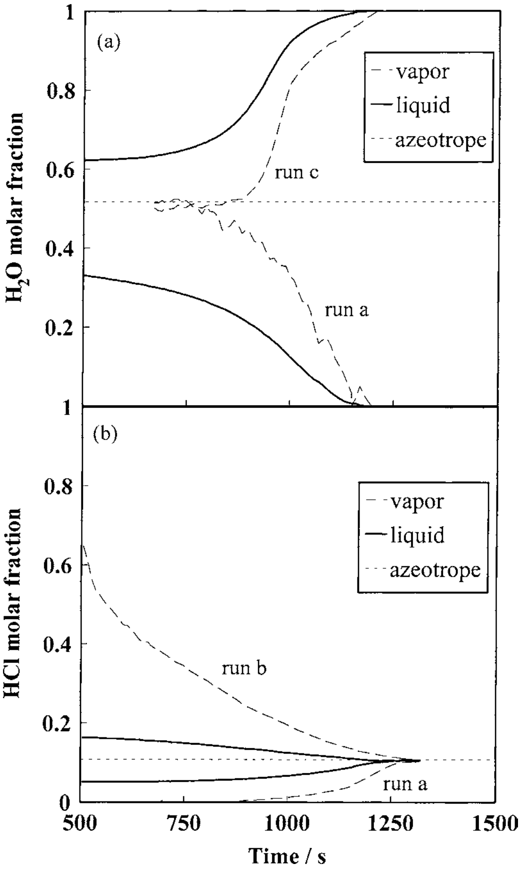

Fig. 2. Molar composition of evolved vapor and residual liquid as a function of time during the vaporization of binary mixtures (initial compositions and conditions of TG runs are reported in Table 2). (a) Water–1,4-dioxane (runs a, c) and (b) HCl–water (runs a, b).

a boiling point of 87.8 °C at atmospheric pressure. The molar compositions of the vapor evolved and of the residual liquid, calculated by the above described procedure, are reported in Fig. 2(a) for two different runs. The sample used in run a had an initial HVC content (35.4 mol% water) lower than that of the azeotropic mixture, while the sample used in run c had an initial HVC content (62.4 mol% water) higher than that of the azeotropic mixture. The figure shows that, as expected, vapor and liquid compositions as a function of time and temperature have a completely different behavior. In run a, the initial vapor composition is very close to the azeotropic one, and both the vapor and the liquid progressively enrich in 1,4-dioxane (the LVC). On the other hand, in run c the initial vapor composition is also quite near to the azeotropic one, but both the vapor and the liquid progressively enrich in water, even if this is the HVC of the system. This behavior should not surprise, since the azeotrope acts as a new compound and divides the composition range into two intervals. The first is defined by water concentration below the azeotropic one (as for run a), where 1,4-dioxane is the LVC and the azeotrope behaves as the HVC. The second corresponds to water concentrations above the azeotropic one (as for run c), where the azeotrope behaves again as the HVC but water becomes the LVC.

Differences were observed performing experimental runs on temperature maximum azeotropic systems. The results obtained for the hydrogen chloride–water system are shown in Fig. 2(b). HCl–water is a binary system that presents complete solubility and was chosen as representative of binary homogeneous systems having a temperature maximum azeotrope. As shown in Table 1, the HCl–water system has a temperature maximum azeotrope at 11.1 mol% hydrochloric acid. HCl is the HVC of the system (b.p. = −85 °C) and water is the LVC. The boiling temperature of the azeotropic mixture at atmospheric pressure is 108.6 °C. The molar composition of the vapor evolved and of the residual liquid are reported in Fig. 2(b) for two different runs. The sample used in run a had an initial HVC content (5.13 mol% HCl) lower than that of the azeotropic mixture, while the sample used in run b had an initial HVC content (16.7 mol% HCl) higher than that of the azeotropic mixture. In run a the vapor evolved initially is almost only composed of water, even if this is the LVC of the system. Both the vapor and the liquid progressively enrich in HCl (the HVC), until they approach the azeotropic composition. On the other hand, in run b vapor is richer in HCl (the HVC) than the liquid, and both the vapor and the liquid progressively enrich in water (the LVC), approaching the azeotropic composition. Also in this case, the azeotrope splits the composition range into two intervals. In the one where hydrogen chloride concentration is below the azeotropic one, the azeotrope behaves as the LVC and water is the HVC. Where hydrogen chloride concentration is above the azeotropic one, the azeotrope behaves again as the LVC and this time HCl is the HVC.

From data as those reported in Figs. 1 and 2, the weight loss of the sample on the basis of FTIR data

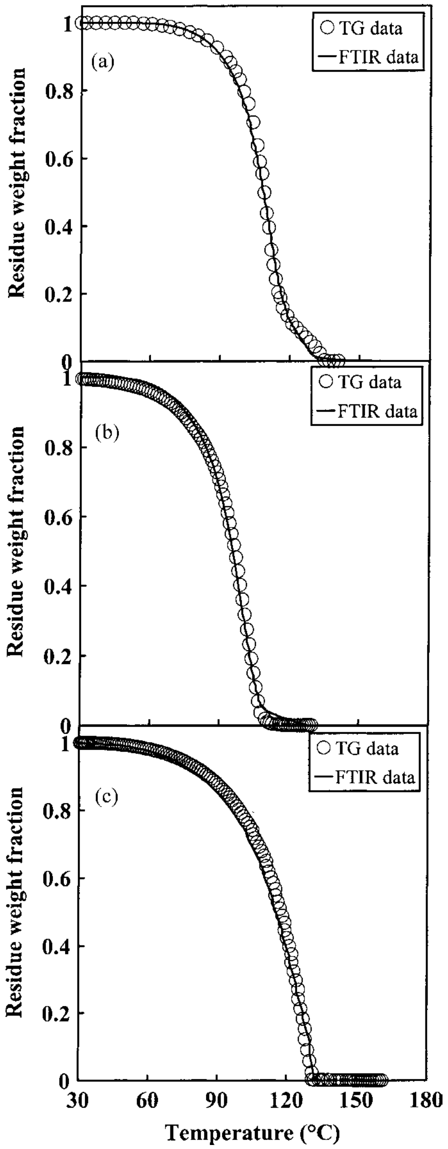

Fig. 3. Weight loss during TG-FTIR runs obtained from TG data and from the analysis of FTIR spectra. (a) Water–DMF (run b); (b) water–1,4-dioxane (run a) and (c) hydrogen chloride–water (run b).

was calculated. This was possible multiplying the molar amounts of the components obtained from Eq. (7) by the respective molecular weights. Typical results obtained from the analysis of data as those reported in Figs. 1 and 2 are reported in Fig. 3, where a comparison is made with experimental TG data. As shown in the figure, a sufficiently good accordance was found between weight loss measured by TG and calculated from FTIR data, thus confirming the validity of the approach. In particular, the results reported in Fig. 3 show that the quantitative FTIR data obtained for the composition of vapor evolved in the TG run are sufficiently reliable, at least allowing the estimation of the overall composition of the vapor evolved and of the residual liquid. Comparable results were obtained from the analysis of the data obtained with the other tested mixtures.

3.3. Separability of the binary systems

In binary homogeneous mixtures, the relative volatility is always higher than unity in the absence of azeotropes. In minimum temperature binary azeotropic systems, relative volatility assumes values above unity when the composition of the mixture is such that the HVC:LVC ratio is lower than the azeotropic one. In maximum temperature azeotropic systems, the value of relative volatility is above unity when the composition of the mixture is such that the HVC:LVC ratio is higher than the azeotropic one.

A qualitatively similar behavior is expected for the separability coefficient defined by Eq. (10), if the experimental conditions during TG-FTIR runs reasonably approach equilibrium conditions. From the molar fraction-time profiles as those shown in Figs. 1 and 2, plots reporting the evolution of the separability coefficient during the vaporization run could be easily obtained. Some of the results are shown in Figs. 4–7. Fig. 4 reports the results obtained with two well-known zeotropic systems. Fig. 4(a) shows the values of σ as a function of liquid composition obtained during two different vaporization runs on water–DMF samples. Values of the separability coefficient of water (the HVC) with respect of DMF (the LVC) between four to six were obtained over a range of liquid molar compositions comprised between 0.1 and 0.75. The large values of the separability coefficient suggest a good degree of separability of this mixture, in other words it means that water can be easily separated from DMF by a distillation process. As shown in Fig. 4(b) similar trends were obtained with the water–NMP system. Values of the separability coefficient of water (the HVC) with respect to NMP (the LVC) between 20 and 30 were obtained

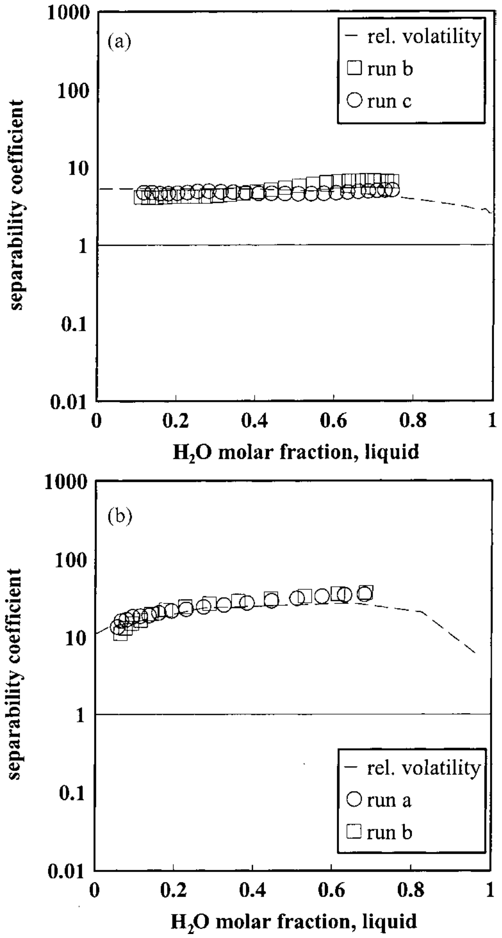

Fig. 4. Experimental values of separability coefficient as a function of liquid composition obtained during the vaporization of (a) water–DMF and (b) water–NMP mixtures compared to relative volatility values computed from literature data (details on experimental runs are reported in Table 2).

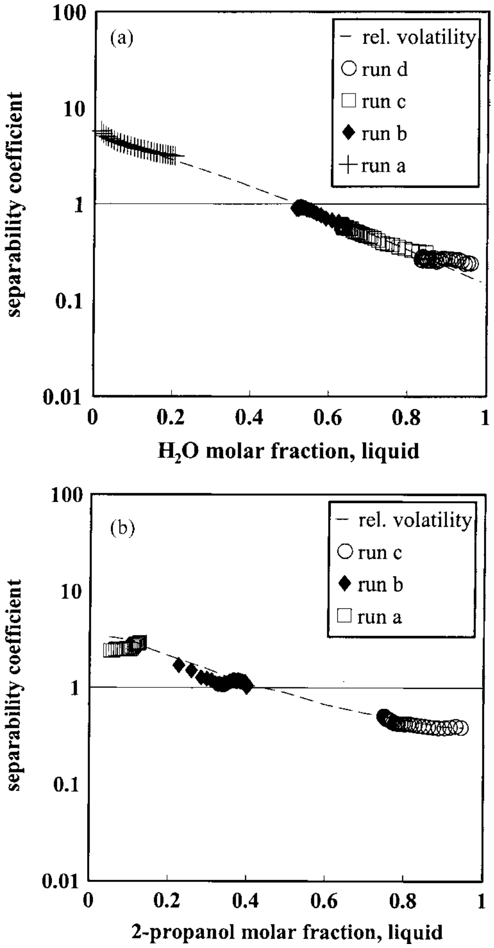

Fig. 5. Experimental values of separability coefficient as a function of liquid composition obtained during the vaporization of (a) water–1,4-dioxane and (b) 2-propanol–1,2-dichloroethane mixtures compared to relative volatility values computed from literature data (details on experimental runs are reported in Table 2).

over the range of liquid molar compositions obtained during two different vaporization runs. The TG-FTIR experiments show also that it is easier to separate water from NMP than from DMF.

Fig. 5 reports the results obtained with an aqueous and a non-aqueous azeotropic system, both having a temperature minimum azeotrope. Fig. 5(a) shows the results obtained from different runs carried out on the water–1,4-dioxane system. Firstly, the figure shows that the value of the separability coefficient of water (the HVC) with respect to 1,4-dioxane (the LVC) equals the unity for a liquid molar concentration of about 52% which represents the point of azeotropism of this system at atmospheric pressure. Secondly, the results of vaporization runs on mixtures with initial composition above the azeotropic one (runs b, c and d), show, as expected, values of the separability coefficient below the unity. This is in accordance with the results reported in Fig. 2(a) (see run c) showing that during the vaporization the molar composition of the residual liquid progressively moves away from the azeotropic point towards pure water, even if this is the HVC. On the other hand, the results of vaporization run a (initial sample composition less than 51.7 mol%

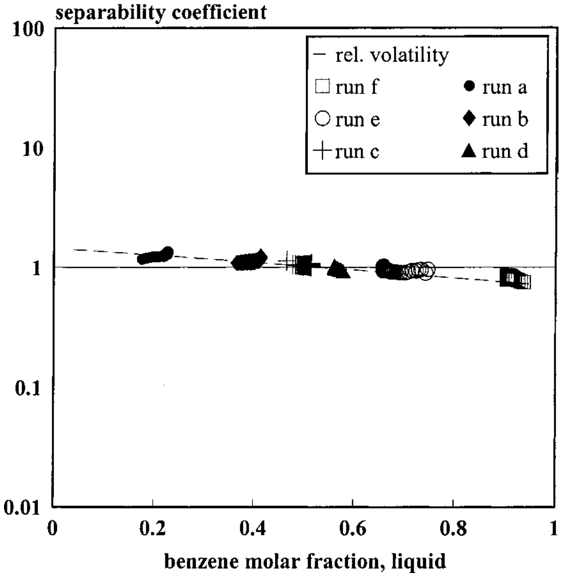

Fig. 6. Experimental values of separability coefficient as a function of liquid composition obtained during the vaporization of benzene–cyclohexane mixtures compared to relative volatility values computed from literature data (details on experimental runs are reported in Table 2).

of water) show that the values of the separability coefficient are above unity, thereby indicating that the vapor is richer in the HVC than the liquid.

A qualitatively similar behavior was obtained with the 2-propanol–1,2-dichloroethane system, as shown in Fig. 5(b). The separability coefficient equals the unity for a liquid concentration of 47 mol% 2-propanol, which as shown in Table 1 corresponds to the point of azeotropism of this system at atmospheric pressure. As expected for a system having a temperature minimum azeotrope, the separability coefficient is above unity for liquid compositions below the azeotropic one and below unity for liquid compositions above the azeotropic one.

To study the reliability of the method, experiments were performed also on a rather critical system such as the benzene–cyclohexane system. As shown in Table 1, the system has a minimum azeotrope at 53.8 mol% benzene and has a very limited temperature difference (<3 °C) between the boiling temperatures of the azeotrope and of the pure components. The results reported in Fig. 6 show that, as expected, the separability coefficient of benzene with respect to cyclohexane equals the unity at the azeotropic point. Moreover, the results show that also for this system reasonable data were obtained for the separability coefficient as a function of liquid composition, i.e. values above the unity for compositions below the azeotropic one and values below the unity for compositions above the azeotropic one. The results also reveal that within the range of composition either below or above the azeotrope, the degree of separability is very low. The figure shows in fact that the values of σ remain significantly close to the unity over a wide range molar composition of the liquid.

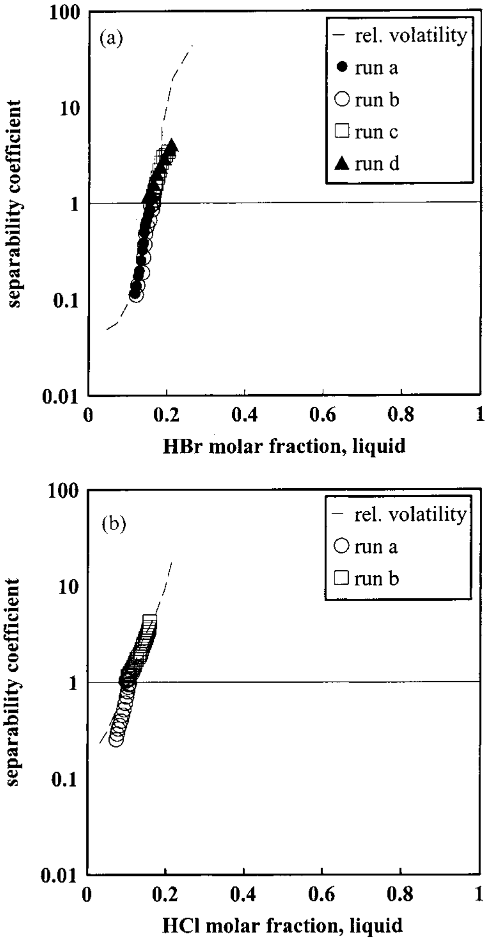

Fig. 7. Experimental values of separability coefficient as a function of liquid composition obtained during the vaporization of (a) hydrobromic acid and (b) hydrochloric acid solutions compared to relative volatility values computed from literature data (details on experimental runs are reported in Table 2).

Finally, the results obtained with two azeotropic systems having a temperature maximum azeotrope are reported in Fig. 7. Fig. 7(a) shows the values of the separability coefficient as a function of liquid composition obtained during four different vaporization runs on HBr–water samples. Fig. 7(b) shows similar results obtained during two vaporization runs on HCl–water samples. The behavior of the separability coefficient with respect to liquid compositions was found to agree with the qualitative behavior expected for binary systems with a temperature maximum azeotrope. In fact, values of the separability coefficient below the unity, equal to unity and above the unity were obtained for liquid compositions, respectively, below, equal to and above the azeotropic one.

3.4. Comparison of the separability coefficient to relative volatility data

The trend of the separability coefficient defined within this study in order to interpret the results of TG-FTIR vaporization runs was found to agree with the qualitative behavior that should be expected for the vapor–liquid enrichment in the binary systems considered. However, it is of fundamental importance to verify if also a quantitative correspondence exists. Thus, it is interesting to compare relative volatility data for the binary systems considered herein to the experimental values of the separability coefficient. To this purpose, in Figs. 4–7 comparisons with either literature or predicted data for relative volatility as a function of liquid composition are shown. The sources for the data reported in the figures are listed in Table 1.

Figs. 4–7 show that a sufficiently good accordance is present between the values of relative volatility and those of the separability coefficient. This indicates that the TG-FTIR system reasonably approaches equilibrium conditions during the experimental vaporization runs performed at the heating rates used in the present study. The mean relative error between relative volatility values and the separability coefficient is less than 10% for most of the binary systems studied. Thus, the values of the separability coefficient well represent the actual values of the relative volatility. These results seem to suggest that the TG-FTIR methodology developed in the present study may be useful for a first screening of vapor–liquid enrichment of a binary mixture.

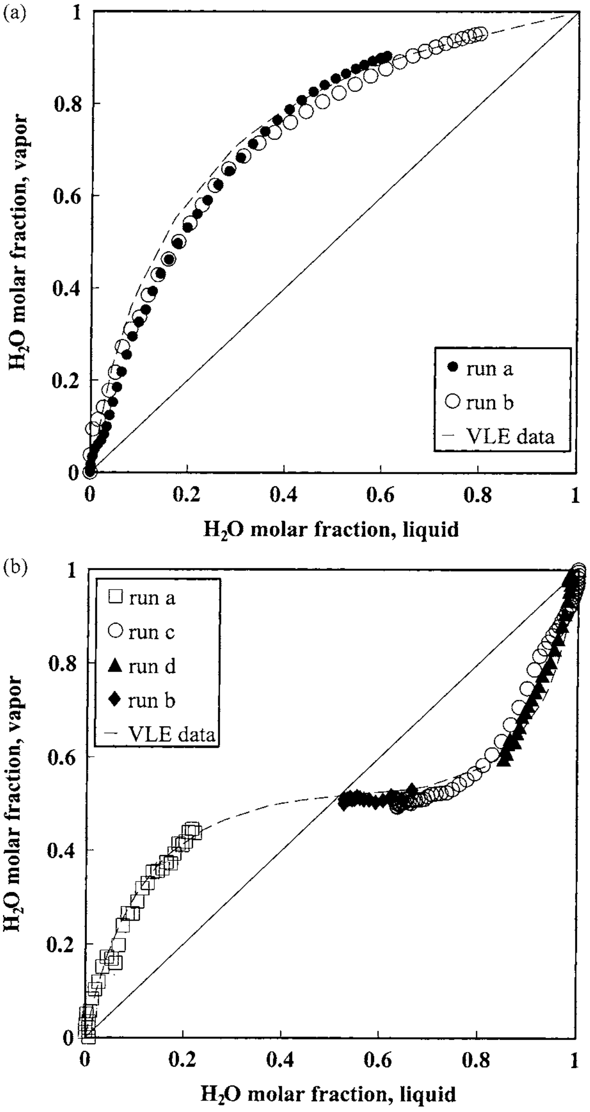

Fig. 8. Experimental values of liquid and evolved vapor compositions obtained during the vaporization of (a) water–DMF and (b) water–1,4-dioxane mixtures compared to equilibrium data (details on experimental runs are reported in Table 2).

A further confirmation comes from the comparison of the molar fractions in the liquid and in the vapor of the more volatile component, calculated from Eqs. (6) and (9), to equilibrium values in *x*–*y* plots.

Some results are reported in Fig. 8 where a comparison with either literature or predicted vapor–liquid equilibrium (VLE) data is also shown. Fig. 8(a) reports some of the results obtained for the water–DMF system. The experimental data obtained by the dynamic TG-FTIR apparatus are in reasonable agreement with the equilibrium data reported in the literature [7]. It must be pointed out that, due to the dynamic configuration of the device, single TG-FTIR experimental runs are able to yield a full set of preliminary data on the approximate VLE compositions. Results reported in Fig. 8(b) for the water–1,4-dioxane system confirm the validity of the method. Also in this case a good correspondence is present between the TG-FTIR data and the equilibrium curve calculated from the azeotropic data using the Margules equation [9]. The results of a vaporization run performed using a sample with initial composition very close to the azeotropic one (run b: 51.9 mol% water) shows that the vapor and liquid compositions remain very similar to the azeotropic ones until the almost complete vaporization of the sample. At the end of the run, the vapor enriches in water following with sufficient accuracy the equilibrium curve. Nevertheless, the possible errors deriving from the dynamic configuration of the apparatus suggest to use the x–y data obtained from TG-FTIR runs with extreme caution. Experimental data in Fig. 8 may be used only as a preliminary screening of vapor–liquid equilibria at an early stage, the application of conventional techniques being necessary to obtain reliable VLE data.

3.5. Limitations in the use of the technique

In the above sections the potentialities of the TG-FTIR technique for the screening of vapor–liquid enrichment were discussed. However, it is also useful to briefly discuss the more important limitations in the use of the technique.

TG-FTIR experiments 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 temperature may not be studied, as well as thermally unstable mixtures with high bubble point.

The absence of sample stirring may be another limitation of the technique in the present experimental configuration. However, the sample quantity is very small and natural convection induced in the liquid by heat transfer is likely to enhance liquid bulk homogeneity when completely miscible systems are investigated. Thus it can be assumed that sample inhomogeneities, if present, have a limited influence on the results. This cannot be stated for heterogeneous systems. These systems are characterized by a light phase stratified on a heavy phase and an efficient stirring would be necessary. Hence, the methodology can only be reliably applied to homogeneous systems using conventional devices.

Commercial devices do not allow positioning a thermocouple inside the sample, that instead would provide more accurate measurement of sample temperature during evaporation. However, the analysis of heat transfer resistances in a TG device indicate that the main heat transfer resistance is that between the gas and the crucible. Hence, no relevant temperature differences are likely to arise between the crucible and its content. Thus, it is believed that thermocouple temperature well represents that of the liquid.

Finally, configuration of experimental runs is dynamic, and evaporation takes place in an open system: thus the separability coefficient data obtained may only be an approximation of the actual values of relative volatility.

4. Conclusions

The methodology developed, based on the analysis of TG-FTIR data, yields a preliminary indication on the separability of binary homogeneous systems. The separability coefficient that may be obtained from the analysis of experimental runs corresponds well with the actual relative volatility data obtained by conventional methods.

The TG-FTIR technique, if used as a preliminary screening tool, has several advantages with respect to conventional methodologies:

- a small amount of sample is required for measurements (less than 30 μl/experiment, corresponding to less than 50 mg by weight for the mixtures examined in the present work);
- safety and disposal problems associated to conventional methods are drastically reduced, due to the size of sample required;
- the technique provides a ready identification of the presence and the indicative composition of azeotropic points;
- the dynamic configuration of the technique allows the separability coefficient to be obtained as a

function of liquid composition, hence the technique provides a straightforward indication of the separability of mixtures;
- the technique uses an internal calibration method;
- FTIR analysis of vapor phase may also allow the identification of impurities or decomposition products that may be formed during the vaporization runs.

However, the TG-FTIR method may only be applied to binary systems where the two components are completely miscible and the vapor phase IR spectrum of each component contains a region reasonably free of contributions from the other component unless deconvolution techniques are used. Moreover, due to the dynamic configuration of experimental runs, the separability coefficient data obtained should only be considered an approximation of the actual values of relative volatility.

Although the application of conventional techniques is necessary to obtain reliable quantitative data for relative volatility, this method constitutes a straightforward approach for the preliminary screening of vapor–liquid enrichment tendency of binary systems.

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