

Use of inverse gas chromatography to account for the pervaporation performance in the microemulsion breakdown[☆]

Amel Hadj-Ziane^a, Saâd Moulay^{a,*}, Jean Paul Canselier^b

^a *Laboratoire de Chimie-Physique Moléculaire et Macromoléculaire, Faculté des Sciences de L'Ingénieur, Département de Chimie Industrielle, Université Saâd Dahlab de Blida, Route de Soumâa, B.P. 270, Blida 09000, Algeria*

^b *Laboratoire de Génie Chimique, (UMR CNRS5503) ENSIACET/INP Toulouse, 5, Rue Paulin Talabot, 31106 Toulouse, France*

Received 1 June 2005; received in revised form 9 July 2005; accepted 13 July 2005

Available online 10 August 2005

Abstract

Mass transfer phenomenon that occurs in the pervaporation process when applied to the microemulsion breakdown, was confirmed by the results of inverse gas chromatography. The stationary phase for this study was polydimethylsiloxane (PDMS), a hydrophobic polymer employed as a membrane in the pervaporation technique. The retention times of the different molecule probes (toluene, cyclohexane, and *n*-butanol) gave an insight into the extent of the interactions between each of these molecules and the stationary phase; these molecules were the components of the two microemulsions in study. The infinite dilution conditions allowed to determine the thermodynamic and the chromatographic parameters γ^∞ (the infinite dilution activity coefficient), the Flory-Huggins parameter interactions χ_{12}^∞ , and V_g^0 (the specific retention volume), respectively. The magnitudes of the latter parameters threw some light on the permselectivity of the membrane in the pervaporation operation.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Inverse gas chromatography; Interaction parameters; Pervaporation; Microemulsion; PDMS membrane

1. Introduction

Pervaporation has been vastly recognized as an energy-saving process to separate organic components from aqueous or organic mixtures [1,2]. In this line, the recovery of organic compounds from wastewater has gained a special attention [3]. Lately, we applied this technique to break down a microemulsion, a highly ordered system [4–6], to monitor the oxidation of primary alcohols [7], and to separate azeotropic mixtures [8]. Its use to control some equilibrated organic reactions was claimed [9]. In the pervaporation operation, as depicted in Fig. 1, the feed mixture is maintained in contact with the upstream side of a dense membrane and the

permeate (or the pervaporate) is continuously removed from the downstream side of the membrane in vapor state by a vacuum pump. The used membrane would alter the vapor–liquid equilibrium (VLE).

As unanimously believed, the membrane remains indubitably the basic key component for the pervaporation performance. Of the aspects of the membrane integrity, the chemical nature in terms of organic functional groups within the backbone or as pendent moieties, hence hydrophobicity and hydrophilicity and in-between, determines its effectiveness in the pervaporation process; for example, the polyvinylalcohol membranes are more hydrophilic due to the hydroxyl groups (OH) present in the polymer structure. The design of a separative membrane destined to the pervaporation process includes: slightly crosslinked polymers, polymer blends, interpenetrating networks, and best of all chemically modified polymers. The latter ones were conveniently made to increase either the hydrophobicity or the hydrophilicity with regard to the aim at applying

[☆] Paper presented to the “1^{er} Colloque Franco-Algérien Sur la Chromatographie”, Algiers, December 1–3, 2004.

* Corresponding author. Tel.: +213 25 43 36 31; fax: +213 25 43 36 31/43 11 64/43 38 64/43 36 39.

E-mail address: saadmoul@yahoo.com (S. Moulay).

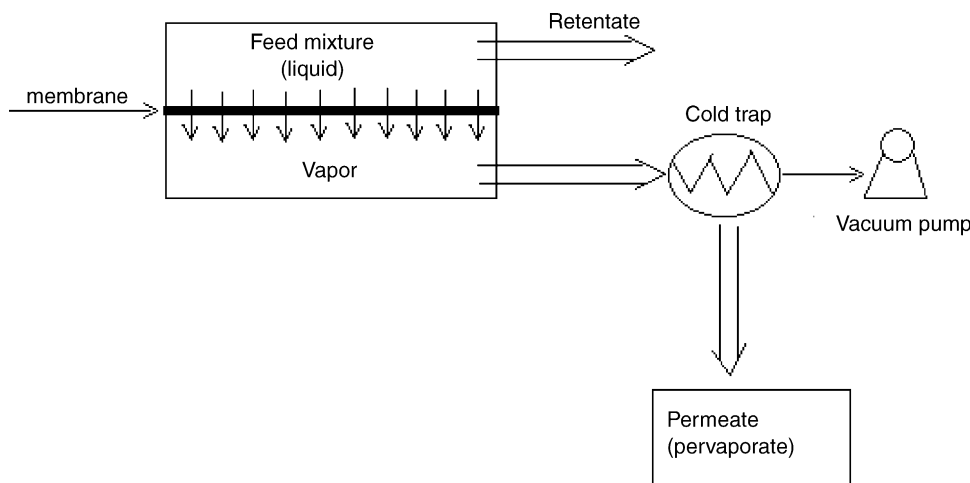


Fig. 1. Basic principles of the pervaporation technique.

the pervaporation. The existing or deliberately introduced functional groups within the membrane will selectively interact with the molecules to be separated.

In the goal of providing a better understanding of the pervaporation performance when operating for the microemulsion breakdown, the extents of the infinite dilution activity coefficient γ^∞ and the interaction parameters of Flory-Huggins, χ_{12}^∞ , were thought to give a better insight. To measure these interaction parameters, the inverse gas chromatography (IGC) was employed because it is a reliable tool for quantifying the extent of interactions. According to the value of the interaction parameter, one can select among others the appropriate membrane for a pervaporation work. One of the many uses of inverse gas chromatography is its application in polymers-related phenomena. In fact, it has been applied to determine the solubility parameters of polymers and oligomers [10,11], the diffusion coefficients in crosslinked polymers [12], the polymer–polymer interaction parameters [13], and the characterization of conducting polymers [14,15].

In our previous work [4–6], polydimethylsiloxane (PDMS) was evaluated as a membrane in the pervaporation for the microemulsion breakdown. For a matter of a better understanding of the results obtained in the pervaporation, PDMS was examined as a sorbent (or solvent) in the inverse gas chromatography study. The molecule probes were toluene, cyclohexane, and *n*-butanol, which were the ingredients of the microemulsions to be collapsed by pervaporation technique. Therefore, the dilution activity coefficient γ^∞ , the interaction parameters χ_{12}^∞ and the thermodynamic factors were experimentally determined by IGC. The results were discussed in light of those of the PDMS swelling and the pervaporation parameters, the total flux and the enrichment factor. In the pervaporation process, the permselectivity is linked to the extent of the interactions of the permeating species with the pervaporative membrane. Such interactions may be indirectly quantified via the magnitudes of the infinite dilution activity coefficients of the sorbates vis-à-vis to the

sorbent (the membrane). Yet, the values are but indicative as the IGC does not really reconstitute the pervaporation process because, in this process, the molecules (probes) are in liquid form in contact with the membrane, but they are in gas phase in IGC. The PDMS used as a solvent in IGC is in rubbery form ($T_g = -123^\circ\text{C}$). Also, the thermodynamic parameters, ΔH_a and ΔG_a , provided by IGC study would give an insight into the pervaporation performance as the absorption of the molecules in study by the PDMS membrane is an important step. Indeed, the composition of the pervaporate depends mostly on the absorption extents of the different components in the feed.

2. Experimental

2.1. Chemicals

Rhodorsil (PDMS/crosslinking agent system, 2% by weight of crosslinking agent) was provided by Rhodia (ex-Rhône-Poulenc). Toluene, cyclohexane, *n*-butanol were supplied by Prolabo, Fluka, and Aldrich, respectively, and were 99% purity (no further purification was done). Water was bidistilled before use. Sodium dodecylsulfate (SDS) was provided from Prolabo and purified by recrystallization from absolute ethanol.

2.2. Pervaporation technique

2.2.1. Apparatus

The pervaporation apparatus used in this work was previously described [8]. It is comprised of the following parts: a stainless steel pervaporation cell (capacity of 125 cm³); a pervaporation pyrex-made receiving set fitted with vapor traps; a primary vacuum pump (10⁻¹ mmHg), Trivac type.

2.2.2. Membrane preparation

A suitable amount of Rhodorsil was spread evenly over a clean teflon-plate surface by means of an appropriate

Table 1
Compositions of the microemulsions (wt.%)

System	Cyclohexane	Toluene	Water	<i>n</i> -Butanol	SDS
I	87	–	1	8	4
II	–	80	2	12	6

applicator. A transparent film was obtained after drying for 24 h at room temperature followed by an annealing at temperature of 50 °C for an additional 8 h. The membrane thickness (20 μm) was measured with a micrometer (Micro-Italiana).

2.2.3. Membrane/pervaporation parameters

The compositions of the two microemulsions to be broken down by the pervaporation technique are compiled in Table 1.

The swelling degrees of the membranes with toluene, cyclohexane, *n*-butanol, and water were determined by the following equation, Eq. (1):

$$S(\%) = \left[\frac{w - w_0}{w_0} \right] \times 100 \quad (1)$$

where w_0 and w are the sample weight before and after swelling. The total mass flux J was provided by the following equation, Eq. (2):

$$J(\text{kg/h m}^2) = \frac{W}{tA} \quad (2)$$

where W is the weight of the condensate (kg), t the trapping time (h) and A the surface area of the membrane (m²); the surface area of the membrane was 26.62 cm².

The enrichment factor β (in a separation of a mixture by pervaporation, the selectivity or the separation factor, α , is more suited) is estimated from the following relation, Eq. (3)

$$\beta = \frac{C_i(\text{pervaporate})}{C_i(\text{retentate})} \quad (3)$$

where C_i is the weight concentration (wt.%) of the preferentially permeating component i , in the pervaporate mixture.

Figs. 2–4 present the swelling extent of PDMS by the different components of the microemulsions, the variations of the total flux J , and the variations of the enrichment factors β , respectively. The enrichment factors given are those of cyclohexane and toluene, the preferentially transported components in Systems I and II.

2.3. Inverse gas chromatography technique

2.3.1. Equipment preparation

Gas chromatography used in this work was the type of Hewlett Packard 5730A fitted with a FID detector and coupled to a Perkin-Elmer integrator (Model LG-100); N₂ was a carrier gas flowing at 3 mL/min and a soap-film meter was employed to measure the gas flow rates. For binary systems, the molecule probes were injected individually with a 10 μL Hamilton syringe. Also, to assess the effect of *n*-butanol, the co-surfactant, on the activities of cyclohexane and toluene, the mixtures of two probes (cyclohexane and

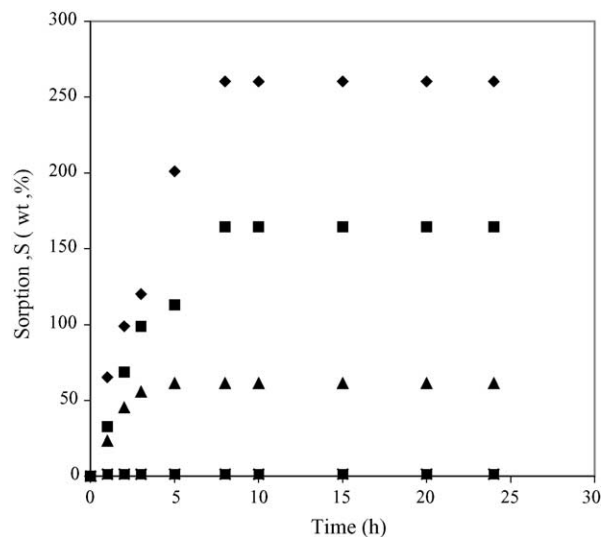


Fig. 2. Variations of the sorption of the PDMS membrane with time by: (◆) cyclohexane; (■) toluene; (▲) *n*-butanol and (●) water. The working temperature was 40 °C.

n-butanol, toluene and *n*-butanol) in ratios based on the compositions given in Table 1 were prepared and injected. These two mixtures are herein designated M_{CB} and M_{TB}, respectively. The injection- and detector-port temperatures were set at 180 °C. The column was prepared as follows:

1. Chromosorb W was employed as a stationary phase solid support (80 mesh, specific area of 1 m²/g). Prior to use, it was deactivated with an acidic washing followed by a treatment with dimethyldichlorosilane (DMCS).
2. *Impregnation of the solid support*: Approximately 0.2 g of polymer (the PDMS employed was the non-crosslinked one) was dissolved in 30 mL of ethyl acetate, and the solution was placed into a 250 mL round-bottomed flask. After addition of 2 g of the solid support, the slurry was well

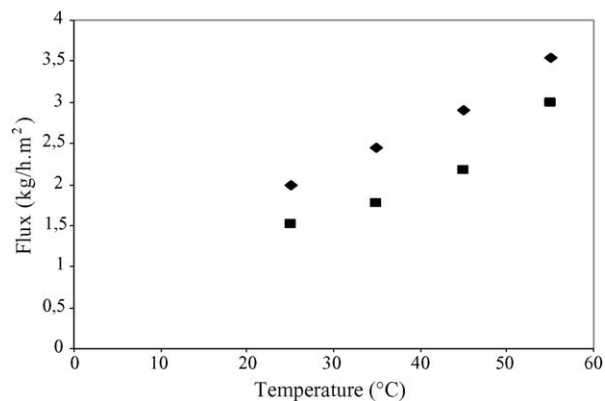


Fig. 3. Variations of the total flux J as a function of temperature: (■) the microemulsion system I and (◆) the microemulsion system II. The operation time was 3 h; the membrane thickness was 20 μm.

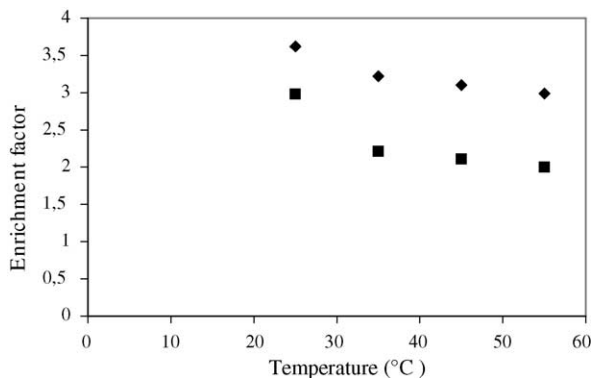


Fig. 4. Variations of the enrichment factor as a function of temperature: (■) cyclohexane in the microemulsion system I and (◆) toluene in the microemulsion system II. The operation time was 3 h; the membrane thickness was 20 μm .

swirled before evaporation of the solvent to dryness by means of a rota-evaporator. Afterwards, the impregnated support was further dried in vacuo in a drying-oven for 48 h. The dried solid was then sieved before the following step.

3. *Column packing*: A 1 m \times 4.4 mm stainless steel column was thoroughly filled with the impregnated solid support. To ensure a homogeneous packing, the filling operation was secured with an electric vibrator.
4. *Column conditioning*: After the packing process, the column was subjected to heat at a temperature of 200 °C for 48 h under a gas carrier flow rate of 3 mL/min.

2.3.2. Inverse gas chromatography parameters

The specific retention volume V_g^0 , the normalized volume of the carrier gas necessary to elute the molecule probe (solute) i out of the column, was calculated using the following equation, Eqs. (4) and (5):

$$V_g^0 = \frac{jF(t_i - t_a)}{W_s} \frac{273.15}{T_c} \quad (4)$$

$$j = \frac{3(P_{in}/P_{ou})^2 - 1}{2(P_{in}/P_{ou})^3 - 1} \quad (5)$$

where t_i is the measured retention time at maximum peak of the solute i ; t_a the retention time of methane, the non interacting probe. J is the James-Martin pressure drop correction; F the saturated carrier gas flow rate; T_c the column temperature; P_{in} and P_{ou} are the pressures at the inlet and the outlet, respectively.

The variations of $\ln V_g^0 = f(1/T)$ corresponding to the different probes are illustrated in Figs. 5–7.

ΔV_{gC}^0 and ΔV_{gT}^0 herein stand for ΔV_{gC}^0 (cyclohexane) – ΔV_{gC}^0 (n -butanol) and ΔV_{gT}^0 (toluene) – ΔV_{gT}^0 (n -butanol), respectively.

Methane was injected to obtain the dead volume or the reference retention time.

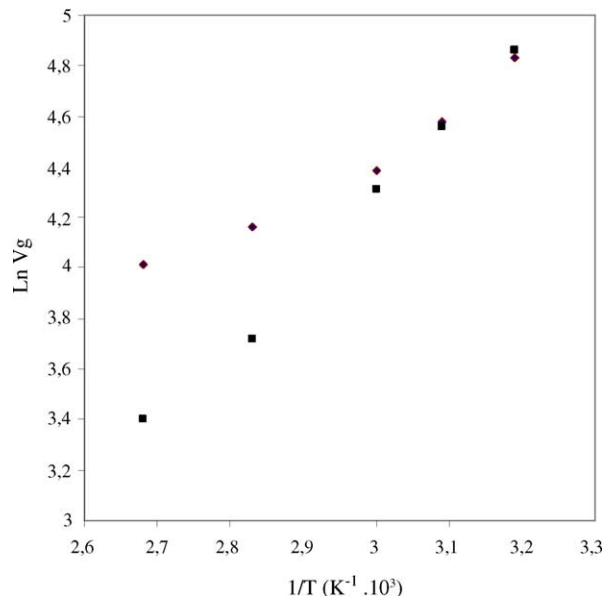


Fig. 5. Variations of $\ln V_g^0 = f(1/T)$: (◆) cyclohexane in a binary system and (■) cyclohexane in the $M_{CB}/PDMS$ system, the cyclohexane/ n -butanol mixture.

The infinite dilution activity coefficient of the molecule probe i , γ_i^∞ , was estimated from the solute retention volume using the following equation [16], Eq. (6):

$$\ln(\gamma_i^\infty) = \ln \left(\frac{273.15R}{M_s P_i^s V_g^0} \right) - \frac{P_i^s (B_{ii} - V_i)}{RT} \quad (6)$$

where R is the universal gas constant, M_s the molar volume of the solute i ; P_i^s the saturation pressure of solute i at temperature T ; B_{ii} the second virial coefficient of the probe, its values at the different temperatures were taken from [17].

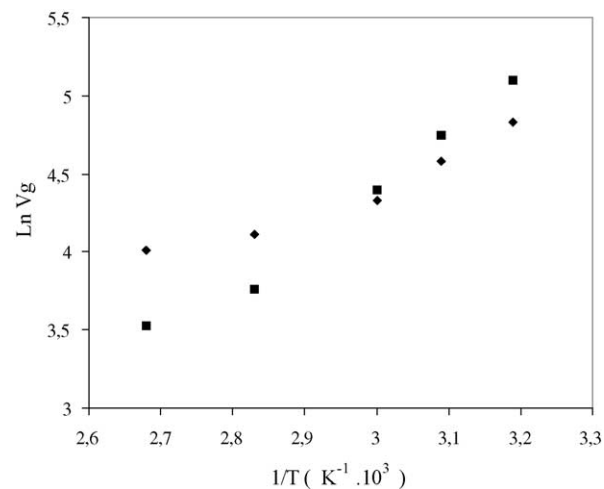


Fig. 6. Variations of $\ln V_g^0 = f(1/T)$: (◆) toluene in a binary system and (■) toluene in the $M_{TB}/PDMS$ system, the toluene/ n -butanol mixture.

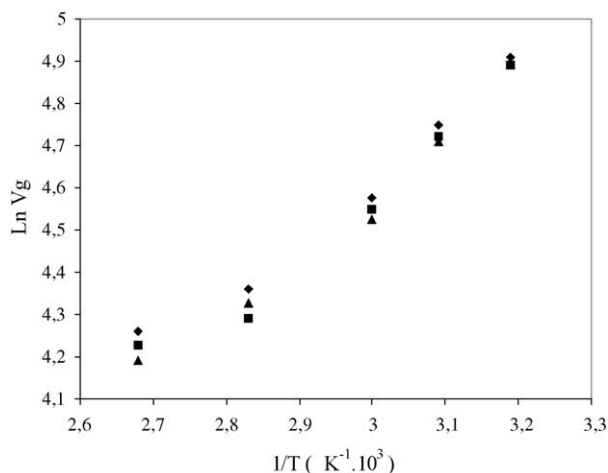


Fig. 7. Variations of $\ln V_g^0 = f(1/T)$: (◆) *n*-butanol in a binary system; (■) *n*-butanol in the $M_{CB}/PDMS$ system, the *n*-butanol/cyclohexane mixture and (▲) *n*-butanol in the $M_{TB}/PDMS$, the *n*-butanol/toluene mixture.

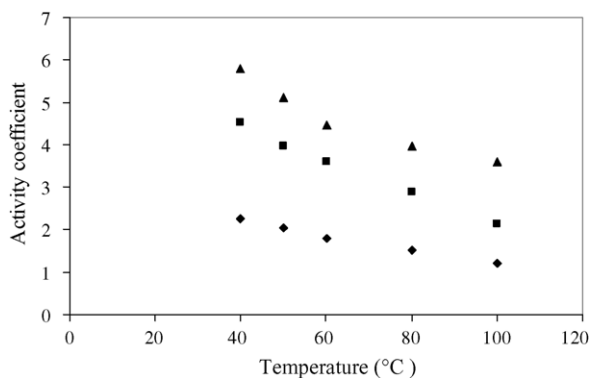


Fig. 8. Variations of the infinite dilution activity coefficients with temperature: (◆) cyclohexane; (■) toluene and (▲) *n*-butanol.

The Flory-Huggins interaction parameter, χ_{12}^∞ , was computed from the following relation [18], Eq. (7):

$$\chi_{12}^\infty = \ln \gamma_i^\infty - 1 \quad (7)$$

The systems considered in this study were: the binary cyclohexane/PDMS, toluene/PDMS, and *n*-butanol/PDMS; $M_{CB}/PDMS$ and $M_{TB}/PDMS$.

The variations of γ_i^∞ for the different sorbates are presented in Fig. 8.

3. Results and discussion

3.1. Sorption/pervaporation

The sorption of the different microemulsion components by PDMS membrane is depicted in Fig. 2 as a function of time. It shows that the membrane swells far better in cyclohexane and toluene, the oily components, than in *n*-butanol.

That is, the sorption of cyclohexane and toluene are nearly four- and three-fold that of *n*-butanol, respectively. After 8 h, the saturation was reached and the optimal sorptions were found to be 280, 180, and 60% for cyclohexane, toluene, and *n*-butanol, respectively. These sorption differences are in accord with the solubility parameter (δ_i) approach which states that the closer the solubility parameter of a component to that of the membrane, the better its affinity towards it or the better is its swelling, (or utmost its solubility). Indeed, the solubility parameter difference $\Delta\delta(\delta_{PDMS} - \delta_i)$ are 0.9, 1.6, and 4.1 for cyclohexane, toluene, and *n*-butanol, respectively. The solubility parameters are 7.3, 8.2, 8.9, 11.4 (cal cm³)^{1/2} for PDMS, cyclohexane, toluene, and *n*-butanol, respectively [19].

The variations of the pervaporative parameters, the total flux J and the enrichment factors β , for the breakdown of the microemulsions I and II, are plotted in Figs. 3 and 4 as a function of temperature. The pervaporation operation process was applied after attaining the permanent regime, that is the optimal sorption of the microemulsions by PDMS membrane. It is worth indicating that the microemulsions I and II were thermally stable at temperatures up to 80 °C, and, therefore, their collapse is totally due to the pervaporation regime. As can be noticed, the total flux increased with temperature for both systems but a relatively slightly greater increase for system I. The enrichment factors β declined with temperature; yet, the extent of decline was more significant for system II than for system I.

3.2. IGC results

The inverse gas chromatography technique was used as an alternative to validate our results obtained in the microemulsion breakdown by the pervaporation technique because both techniques involve the sorption–diffusion–desorption phenomenon; yet, the overall processes are different.

The strategy of this present study was first to assess the interactions within a binary system consisting of a solute (molecule probe) and the solvent (polymeric stationary phase), and second to consider those within $M_{CB}/PDMS$ and $M_{TB}/PDMS$ systems. The working temperatures were between 40 and 100 °C. The different results are gathered in Tables 2 and 3 (only results for the lowest and highest temperatures are given). Figs. 5–7 show the different plots of $\ln V_g^0 = f(1/T)$.

The profile of the plot $\ln V_g^0 = f(1/T)$ is claimed to be a straight line with a positive slope for temperatures higher than the glass transition temperature, T_g , of the polymer used as a sorbent. In our case, the working temperatures were higher than the T_g of PDMS (−123 °C) and the results indicate that expected straight lines were observed between 40 and 60 °C. However, a slight deviation from the straight line occurs at temperatures higher than 80 °C for all probes in all systems studied. The results (Tables 2 and 3) showed that *n*-butanol in M_{CB} and M_{TB} affects the activities of cyclohexane and toluene but not to a great extent. It is interesting

Table 2
Thermodynamic and chromatographic results for the sorbates: cyclohexane and *n*-butanol

	Binary system				M _{CB} /PDMS system			
	Cyclohexane		<i>n</i> -Butanol		Cyclohexane		<i>n</i> -Butanol	
<i>T</i> (°C)	40	100	40	100	40	100	40	100
<i>V_g</i> (mL/g)	125.63	55.69	115.8	48.2	129.66	54.36	134.1	67.3
γ_i^∞	2.25	1.2	5.80	3.6	2.10	1.35	4.98	3.51
χ_{12}^∞	-0.19	-0.81	0.75	0.28	-0.25	-0.69	0.60	0.25
ΔH_a (kJ/mole)	-6.31	-6.31	-3.46	-3.46	-8.52	-8.52	-3.63	-3.63
ΔG_a (kJ/mole)	-12.88	-13.37	-12.78	-12.92	-12.96	-13.30	-13.05	-13.96

to note that the retention volumes V_g^0 of cyclohexane and toluene in binary, M_{CB}/PDMS and M_{TB}/PDMS systems (Figs. 5 and 6) did not vary for temperatures lower than 60 °C, but were almost greater in binary systems than in M_{CB}/PDMS and M_{TB}/PDMS for higher temperatures. Although the phenomenon occurred in a gas state, it appears that *n*-butanol refrained the mobility of cyclohexane and toluene to a certain extent. Surprisingly, the retention volume for *n*-butanol was almost unaffected by their presence as shown in Fig. 7. The greater the ΔV_g^0 , the higher is the enrichment factor. Indeed, the ΔV_{gT}^0 was found to be greater than ΔV_{gC}^0 implying that the enrichment factor for the microemulsion of system II would be higher than that for system I. This is in a fair agreement with the results shown in Fig. 4. Overall, the ΔV_g^0 decreased with increasing temperature which explains the decline of β with temperature.

The variations of the infinite dilution activity coefficients γ_i^∞ of the solutes were found to decrease nearly linearly with temperature (Fig. 8) suggesting a higher diffusion at elevated temperatures. This temperature dependence was also reported by Ferreira and Focco [20]. It can be seen that γ_i^∞ (cyclohexane) < γ_i^∞ (toluene) < γ_i^∞ (*n*-butanol) indicating an enhanced solvation of the PDMS macromolecular chains, thus a greater penetration of cyclohexane and toluene in the membrane. The higher diffusion at elevated temperatures would account for the increasing flux depicted in Fig. 3. The interaction parameter of Flory-Huggins, χ_{12}^∞ , varies with temperature in the same fashion as the activity coefficient as the equation Eq. (7) may imply. The χ_{12}^∞ decreased by raising the temperature for all sorbates as the theory predicts [21]. The smaller the χ_{12}^∞ , the better the absorption of the PDMS by the probes, giving an insight into a better diffusion into the membrane. In addition, the smaller the χ_{12}^∞ ,

the better the selectivity, that is the greater the enrichment factor of the molecule. The results of the parameter interaction are in a agreement with the theory which states that $\chi_{12}^\infty = V(\delta_1 - \delta_2)/RT$, where *V*, *R*, δ_1 , and δ_2 are the solute molar volume, the gas constant, the solubility parameters of solute and solvent (polymer), respectively [22]. The smaller the $\Delta\delta = (\delta_1 - \delta_2)$, the smaller the χ_{12}^∞ , and the higher the solvating power of the solute. Thus, the solute that gives the smaller $\Delta\delta$, will have the better affinity towards the membrane as mentioned above.

Because water was also employed as one of the components of the microemulsions, it is enlightening to recall that the γ_i^∞ and the χ_{12}^∞ for water under the same conditions were found to be about 18–19, and 1.90, respectively, at a temperature range of 100–120 °C [23]. The above findings would account for, on the one hand, the better sorption of cyclohexane and toluene than *n*-butanol and water as confirmed in Fig. 2, and, on the other hand, the preferential transport of the oily component (cyclohexane and toluene) of a microemulsion through the membrane in the pervaporation operation as can be seen in Fig. 4; the enrichment factors β in cyclohexane and toluene were found greater than one for both systems suggesting a preferential permeation of the oily components over *n*-butanol and water.

Enthalpies of absorption, ΔH_a were calculated from the slopes of the retention diagrams illustrated in these figures, and according to the following equation, Eq. (8):

$$\Delta H_a = -R \left[\frac{\partial \ln V_g^0}{\partial (1/T)} \right] \quad (8)$$

The magnitudes of the enthalpies of absorption given in Tables 2 and 3 also provide an insight into the behavior of

Table 3
Thermodynamic and chromatographic results for the sorbates: toluene and *n*-butanol

	Binary system				M _{TB} /PDMS system			
	Toluene		<i>n</i> -Butanol		Toluene		<i>n</i> -Butanol	
<i>T</i> (°C)	40	100	40	100	40	100	40	100
<i>V_g</i> (mL/g)	170.35	68.2	115.8	48.2	165.3	65.6	133.1	66.4
γ_i^∞	4.52	2.13	5.80	3.6	4.80	2.16	5.88	3.25
χ_{12}^∞	0.5	-0.24	0.75	0.28	0.56	-0.22	0.77	0.178
ΔH_a (kJ/mole)	-8.69	-8.69	-3.46	-3.46	-7.85	-7.85	-3.63	-3.63
ΔG_a (kJ/mole)	-13.67	-14.00	-12.78	-12.92	-13.60	-13.88	-13.03	-13.91

the membrane towards the components of the microemulsion in study. These values suggest the absence of the specific interactions such as hydrogen bonding between the sorbate and the sorbent. The enthalpies of absorption of cyclohexane and toluene are lower than that of *n*-butanol for the binary, $M_{CB}/PDMS$ and $M_{TB}/PDMS$ systems. This would explain the better sorption of the membrane by cyclohexane and toluene over that by *n*-butanol. While in the binary system, ΔH_a of cyclohexane is higher than that of toluene, in the $M_{CB}/PDMS$ and $M_{TB}/PDMS$ systems, that of toluene is higher. This result could be stemmed from the effect of *n*-butanol. Indeed, the swelling of the membrane was more significant by the cyclohexane-rich micromulsion than by the toluene-borne micromulsion [6].

The free enthalpies of absorption were determined using the following equation [24], Eq. (9) where T_c is the column temperature and ρ is the density of the stationary phase; $\rho_{PDMS} = 0.98$.

$$\Delta G_a = -RT \ln \left(\frac{V_g^0 T_c \rho}{273} \right) \quad (9)$$

The ΔG_a 's at temperatures of 40 and 100 °C for the different sorbates in the binary, $M_{CB}/PDMS$ and $M_{TB}/PDMS$ systems are given in Tables 2 and 3. They fluctuated between -12.78 and -14.00 kJ/mole for all the probes and they decreased but not substantially upon increasing temperature by 60 °C.

4. Conclusion

The inverse gas chromatography study corroborated to a certain extent the results of the microemulsion breakdown by pervaporation technique. The retention volumes, the infinite dilution activity coefficients, the Flory-Huggins interaction parameters, and the enthalpies of absorption for cyclohexane, toluene, and *n*-butanol varied in accord with their sorption by the PDMS membrane used as a solvent in IGC study, and with the variations of the pervaporative factors for the microemulsion collapse, the total flux and the enrichment parameter.

References

- [1] S.M. Zhang, E. Drioli, Sep. Sci. Technol. 30 (1995) 1.
- [2] B. Smitha, D. Suhanya, S. Sridhar, M. Ramakrishna, J. Membr. Sci. 241 (2004) 1.
- [3] F. Lipnizki, R.W. Field, Sep. Purif. Technol. 22–23 (2001) 347.
- [4] T. Aouak, S. Moulay, A. Hadj-Ziane, J. Membr. Sci. 173 (2000) 149.
- [5] Z.A. Hadj-Ziane, S. Moulay, Desalination 170 (2004) 91.
- [6] S. Moulay, A. Hadj-Ziane, N. Bensacia, Sep. Purif. Technol. 44 (2005) 181.
- [7] H. Benguergoura, T. Aouak, S. Moulay, J. Membr. Sci. 229 (2004) 107.
- [8] S. Moulay, T. Aouak, A. Hadj-Ziane, F. Rouabah, M. El Mahdi, J. Soc. Alg. Chim. 10 (2000) 89.
- [9] N. Wynn, Chem. Eng. Prog. 97 (2001) 66.
- [10] E. Morales, J.L. Acosta, Polym. J. 28 (1996) 127.
- [11] P. Choi, T. Kavassalis, A. Rudhin, J. Colloid Interface Sci. 180 (1996) 1.
- [12] P.L. Jackson, M.B. Huglin, Eur. Polym. J. 31 (1995) 63.
- [13] A. Etxeberria, C. Uriate, M.J. Fernandezberridi, J.J. Uruin, Macromolecules 27 (1994) 1245.
- [14] M.M. Chehimi, M.L. Abel, B. Saoudi, M. Delamar, N. Jammul, J.F. Watts, Polimery 41 (1996) 75.
- [15] M.M. Chehimi, M.L. Abel, E. Pigoislandureau, M. Delamar, Synth. Met. 60 (1993) 183.
- [16] D.D. Deshpande, D. Patterson, H.P. Schreiber, C.S. Su, Macromolecules 7 (1974) 530.
- [17] J.H. Dymond, E.B. Smith, The Virial Coefficient of Pure Gases and Mixtures. A Critical Compilation, Oxford Press, Oxford, 1980.
- [18] V. Voelkel, J. Fall, Chromatographia 44 (1997) 34.
- [19] J. Bandrup, E.H. Immergut, Polymer Handbook, third ed., Wiley, New York, 1998.
- [20] O. Ferreira, G.M. Foco, Latin Am. Appl. Res. 33 (2003) 167.
- [21] T.K. Kwei, Macromolecules in solution, in: F.A. Bovey, F.H. Winslow (Eds.), Macromolecules, An Introduction to Polymer Science, Academic Press, New York, 1979, p. 273 (Chapter 4).
- [22] B. Chabert, A. Saint-Yrieix, J. Serpinet, N. Valentin, J. Vial, J. Derminot, Physico-Chimie des Polymères et Surfaces par Chromatographie en Phase Gazeuse, Technique et Documentation, Paris, 1989.
- [23] N. Bensacia, Master thesis, Université Saâd Dahlab, Blida, Algeria, 2002.
- [24] A. Boutboul, F. Lenfant, P. Giampaoli, A. Feigenbaum, V. Ducruet, J. Chromatogr. A 969 (2002) 9.