4412 J. Chem. Eng. Data **2010,** *55,* 4412–4415

Equilibrium Data for the Oxygen + Propane Binary System at Temperatures of (110.22, 120.13, 130.58, and 139.95) K[†]

Deborah Houssin-Agbomson,*,[‡] Christophe Coquelet,[§] Philippe Arpentinier,[‡] Fabrice Delcorso,[‡] and Dominique Richon[§]

Mines ParisTech CEP/TEP Centre Energétique et Procédés, 35 rue Saint Honoré, 77305 Fontainebleau, France, and Air Liquide Claude-Delorme Research Center, 1 chemin de la Porte des Loges, BP 126, 78354 Jouy-en-Josas, France

(P, x) vapor−liquid equilibrium (VLE) data for the (O_2 + C_3H_8) binary system were measured using a "static-analytic" method coupled to a gas chromatograph analysis at temperatures of (110.22, 120.13, 130.58, and 139.95) K. Parameters of a proposed thermodynamic profile were adjusted on the basis of experimental VLE data determined in this work, allowing a complete isothermal phase diagram for this hazardous system to be obtained. The vapor−liquid−liquid equilibrium (VLLE) thermodynamic behavior was predicted by modeling and then confirmed by visual observations. On the basis of this work, solubility values of propane in liquid oxygen can be deduced for both the propane-lean and propane-rich liquid phases at temperatures above the melting temperature of pure propane. The device allowing these data to be measured for such a hazardous mixture is also presented, as are the accuracies of the measurements.

Introduction

Oxygen, nitrogen, and argon are widely used in industry for many and varied applications: metallurgy, chemistry, petrochemistry, refining, energy, electronics, health, etc. These components can be obtained by a cryogenic separation method: the fractionating distillation of atmospheric air. The feed air for air distillation units must be cleaned: before liquefaction, all components that are potentially obstructive at low temperatures (natural or produced by anthropic activities) have to be removed. Despite the use of front-end purification units (FEPUs), some traces of pollutants [CO_2, N_2O, H_2O, and hydrocarbons (in particular propane, ethane, and ethylene)] can remain in the feed air of cryogenic air-separation units (ASUs) and be the origin of drastic dysfunctions of ASU operation. In particular, a more accurate knowledge of propane thermodynamic behavior in potentially hazardous mixtures with oxygen under process operating conditions [temperatures from (92 to 153) K] would improve both evaluation and control of the risks specific to ASUs and their performance.

In the scientific literature, solubility data on hydrocarbons in liquid oxygen are scarce (probably because of the hazardous handling of such flammable mixtures) and not accurate. Since 1957, solubility measurements have been carried out using different operating modes, but unfortunately, the experimental procedures are not sufficiently detailed to estimate the uncertainties of the measured values. A few values of the solubility of propane in liquid oxygen have been published and are listed in Table 1.[1−4]

Important discrepancies between the different published values can be observed. Furthermore, the temperature ranges mentioned in these references are relatively limited [at temperatures from (77 to 90) K] and do not correspond to the whole operation field of ASUs, even if $T = 90$ K is close to important ASU operating conditions. The work of Lassmann (1995) on a developed model (based on a nondescribed equation of state using equilibrium data measured for methane and ethylene with an estimated uncertainty of ± 50 %) that allows solubility values of propane and other hydrocarbons in liquid oxygen from $T =$ (90 to 155) K to be obtained is not seriously exploitable because of the lack of information on the model used and the assumptions and experimental data employed to establish the vapor−liquid equilibrium (VLE) constants and solubility curves.[4]

A preliminary theoretical study on oxygen + propane seems to show a type-III thermodynamic behavior (using the van Konynenburg−Scott classification).[5] Thus, like the nitrogen + propane system, the oxygen + propane binary system certainly exhibits vapor−liquid−liquid (VLL) behavior under particular conditions of equilibrium.[6]

In this work, the phase diagram of the O_2 + C_3H_8 system has been studied at temperatures of (110.22, 120.13, 130.58, and 139.95) K. Thermodynamic modeling allows information on equilibrium properties of this complex system to be obtained up to pure oxygen critical point of 154.58 K.

Experimental Section

Chemicals. Oxygen (CAS no. 7782-44-7) was obtained from Air Liquide with guaranteed mole fraction purity > 0.999995. Propane (CAS no. 74-98-6) was provided by Messer with certified mole fraction purity > 0.9995.

Apparatus. The method used in the present work was of the "static-analytic" type with a rapid online sampler−injector (ROLSI; Guilbot et al.[7]) pneumatic microsampling device and online gas chromatographic analyses.[7,8] A 12 cm^3 Hastelloy C276 equilibrium cell was specifically designed and built in order to withstand pressures up to 300 MPa in case of accidental internal ignition of the oxygen−propane mixture.[6] Inside the cell, temperature and pressure were measured with uncertainties

---

[†] Part of the "Sir John S. Rowlinson Festschrift".

* Corresponding author. E-mail: deborah.houssin@airliquide.com. Fax: +33 139 076 103.

[‡] Air Liquide.

[§] Mines ParisTech.

10.1021/je100574y

Table 1. Literature Values for the Solubility of Propane in Liquid Oxygen

T/K	x(propane)	lit ref	method
77.4	$4.5 \cdot 10^{-2}$	McKinley and Himmelberger, 1957[1]	synthetic optical method
90	$9.8 \cdot 10^{-3}$	Karwat, 1958[2]	unknown experimental method
90.2	$5 \cdot 10^{-2}$	McKinley and Wang, 1960[3]	synthetic optical method
90 to 152	$7 \cdot 10^{-3}$ to $3 \cdot 10^{-2}$	Lassmann, 1995[4]	unknown predictive model

estimated through calibrations to be better than ± 0.02 K and ± 0.18 kPa, respectively.

Sample Analysis. Only liquid-phase composition was analyzed; the vapor pressure of pure propane is lower than 0.08 kPa over the studied temperature range, and thus, the vapor phase is predominantly composed of oxygen. Therefore, only one ROLSI sampler was used, allowing very small and reliable in situ samples to be withdrawn without disturbing the thermodynamic equilibrium; these were directly swept to a gas chromatograph (GC, Varian model 3800) fitted with a HayeSep-T packed column for online analyses of the liquid phase. The uncertainties due to GC calibrations were estimated as twice the standard deviation obtained on the mole number of each component. Thus, the maximal uncertainty in the oxygen composition was lower than 2.1 % whatever the composition range.

Table 2. Bubble Points for the Oxygen (1) + Propane (2) System from (110.22 to 139.95) K at Thermodynamic Equilibrium with Mole Fraction x_1

phases	x_1(expt)	P(expt)/MPa	P(calc)/MPa
		$T = 110.22$ K	
L_1-V	0.095_4	0.268_9	0.2672
	0.106_3	0.290_5	0.2908
	0.131_2	0.338_0	0.3400
	0.161_3	0.398_6	0.3914
	0.181_8	0.431_6	0.4214
	0.228_2	0.484_6	0.4767
	0.274_3	0.507_1	0.5162
L_2-V	0.977_6	0.535_9	0.5389
		$T = 120.13$ K	
L_1-V	0.055_7	0.264_7	0.2696
	0.089_7	0.406_0	0.4100
	0.133_1	0.559_0	0.5641
	0.182_6	0.707_4	0.7073
	0.254_9	0.861_5	0.8602
L_2-V	0.943_0	0.978_5	0.9798
		$T = 130.58$ K	
L_1-V	0.042_7	0.299_1	0.3010
	0.090_9	0.602_2	0.6042
	0.146_6	0.915_7	0.9053
	0.215_3	1.213_0	1.2056
	0.316_9	1.519_2	1.5124
L_2-V	0.925_2	1.695_4	1.6908
		$T = 139.95$ K	
L_1-V	0.026_6	0.246_6	0.2407
	0.215_8	1.658_6	1.6299
	0.419_0	2.435_3	2.4390
L_2-V	0.911_5	2.565_9	2.6023
	0.913_6	2.549_7	2.5856
	0.926_9	2.579_0	2.5875
	0.932_8	2.586_8	2.5059
	0.950_4	2.611_6	2.6231

Table 3. Adjusted Values of Thermodynamic Profile Parameters for the Oxygen (1) + Propane (2) System Based on the NRTL Activity Coefficient Model with a Linear T^{-1} Dependence ($D = B + A \cdot T^{-1}$)

parameter	B	A/K
α_{12}	−0.07	0.00
C_{12}/RT	−1.838	410.35
C_{21}/RT	−1.524	312.91

Equilibrium Data Measurement. Propane was first introduced into the cell, taking into account its thermophysical properties, and then a first amount of oxygen was loaded. Equilibrium was assumed to be reached when the total pressure remained unchanged within ± 0.5 kPa during a period of about 10 min under efficient stirring (tests were carried out to determine this duration). The duration of this operation was generally between (2 and 3) h. Isothermal (P, x) curves representing the liquid-phase composition according to the total pressure were built through several successive oxygen loadings, each being followed by GC analysis.

Results and Discussion

Modeling. In order to represent the experimental VLE behavior of the oxygen + propane binary system, a "Φ−Φ" approach using the Peng−Robinson (PR) equation of state (EoS) was considered.[9] The α function chosen for characterizing molecular attractions was the Mathias−Copeman α function.[10] Three parameters of this function were adjusted on the basis of experimental data to better represent the vapor pressure of the pure compounds than the standard one developed by Peng and Robinson; good accuracy of the vapor pressures is important for modeling of type-III equilibria. The MHV2 mixing rule was employed in order to combine the advantages of the EoS approach and those of the nonrandom two-liquid (NRTL) activity coefficient model referenced to infinite pressure.[11−13]

Results. (P, x) data obtained over a large range of propane concentrations at thermodynamic equilibrium are presented in Table 2. These data were employed to adjust the binary interaction coefficients C_{12} and C_{21} and the nonrandomness parameter α_{12} of the NRTL activity coefficient model used for equilibrium modeling in the thermodynamic profile previously described. First, parameter adjustment was performed isotherm by isotherm, and this preliminary work showed a significant temperature dependence of the binary interaction coefficients. Next, in order to improve the modeling, the binary interaction parameters were adjusted (with temperature dependence) using the whole experimental data set, keeping the nonrandomness

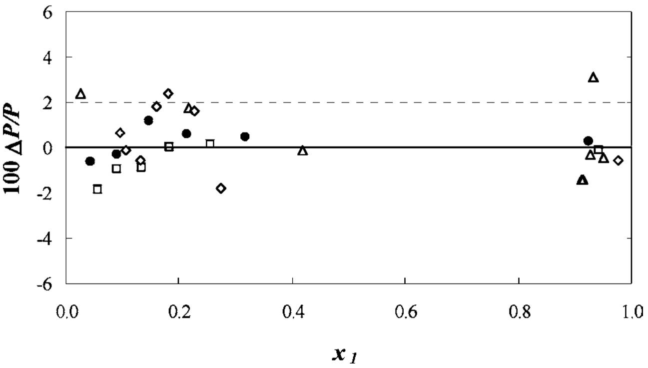

Figure 1. Liquid-phase composition (x_1) dependence of the relative deviation $\Delta P/P = [P(\text{expt}) - P(\text{calc})]/P(\text{expt})$, where P(expt) is the experimental pressure and P(calc) was obtained with the PR EoS using the adjusted parameters from Table 3: ◇, $T = 110.22$ K; □, $T = 120.13$ K; ●, $T = 130.58$ K; △, $T = 139.95$ K.

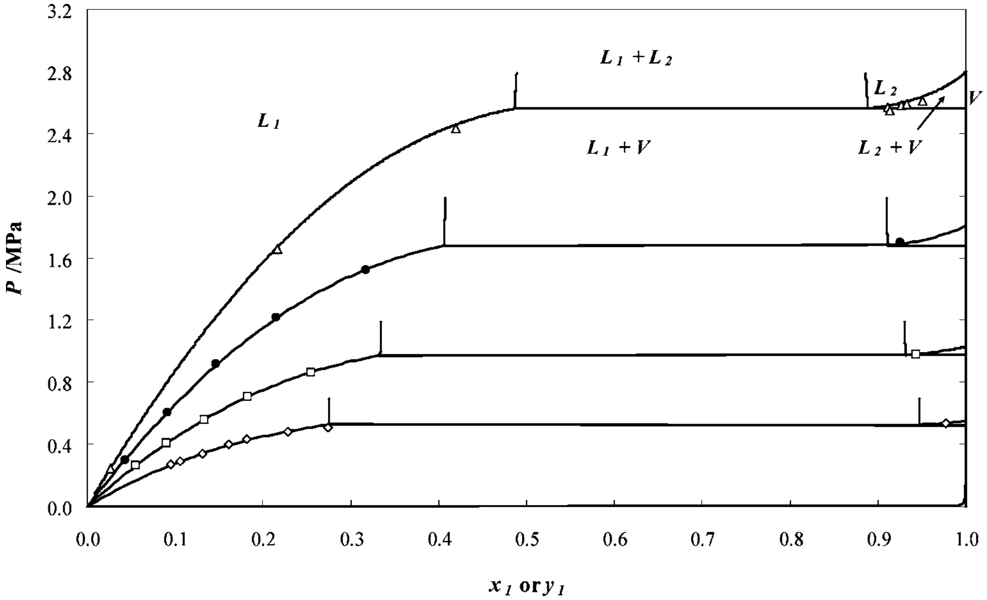

Figure 2. (P, x, y) isothermal phase diagrams for the O_2 (1) + C_3H_8 (2) system. Experimental data: ◇, $T = 110.22$ K; □, $T = 120.13$ K; ●, $T = 130.58$ K; △, $T = 139.95$ K. Solid lines are VLLE diagrams calculated using the PR EoS. L_1, C_3H_8 (2)-rich liquid phase; L_2, C_3H_8 (2)-lean liquid phase; V, vapor phase.

parameter constant (see the values in Table 3). Results of the modeling for $T = (110.22$ to $139.95)$ K are also presented in Table 2 through the calculated pressures P(calc) associated with the measured liquid compositions x_1. Figure 1 shows more precisely the relative deviation between the experimental pressure, P(expt), and the calculated pressure, P(calc), as a function of the measured liquid composition x_1. Good agreement between the experiments and modeling was observed: the bias in the pressure was less than 0.2 %, and the average absolute deviation was around 1 %.

The described model was used to determine the complete phase diagrams for the four studied temperatures (see Figure 2). A type-III thermodynamic behavior in the van Konynenburg−Scott classification[5] (i.e., a VLL equilibrium) was highlighted by calculation. This particular behavior was observed previously by Houssin-Agbomson et al.[6] and other authors for the nitrogen + propane binary system under cryogenic conditions. Additional experiments were performed using another kind of equipment allowing a qualitative analysis of phases to be made by direct visualization at atmospheric pressure and thermodynamic equilibrium. These later tests confirmed the coexistence of three phases under certain conditions of propane concentration: one vapor phase, one propane-rich liquid phase (the upper liquid layer), and one propane-lean liquid phase (the lower liquid layer) (see Figure 3).

Solubility values under vapor−liquid−liquid equilibrium (VLLE) conditions can be deduced from this work for the two coexisting liquid phases (the oxygen-rich and -lean liquid phases). On the basis of modeling, the two-liquid phase region diminishes with increasing temperature, and in the oxygen-rich liquid phase, which corresponds to the ASU industrial context, the propane solubility limit increases (see the calculated values in Figure 4). The solubilities of propane in liquid oxygen as a function of temperature over the temperature range (90 to 140) K can be represented by a simple equation:

$$\ln x_2 = -1.207 - \frac{154.32\ \mathrm{K}}{T} \qquad (1)$$

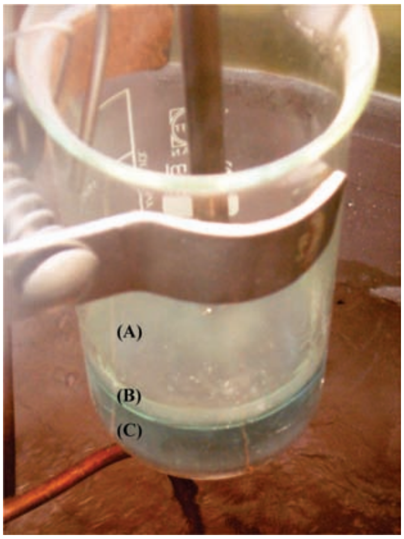

Figure 3. Picture of the vapor−liquid−liquid equilibrium for O_2 + C_3H_8 at atmospheric pressure at a temperature of about 90 K: (A) vapor phase; (B) propane-rich liquid phase; (C) propane-lean liquid phase.

where x_2 is the propane mole fraction solubility and T is the temperature; the data have a bias of −0.1 % and an average absolute deviation of around 4 %.

Discrepancies between the cited literature and our solubility results in the oxygen-rich liquid phase were observed. Overall, the data available in the scientific literature underestimate the solubility of propane in the oxygen-rich liquid phase in comparison with our work, as shown in Figure 5. Karwat's value[2] of the solubility of propane in the oxygen-rich liquid phase (0.98 % at $T = 90$ K) is not consistent with solubility-versus-temperature trend determined by our study; the solubility is underestimated compared to our value. The McKinley and Wang datum published in 1960[3] is consistent with values obtained by extrapolation of our model to lower temperatures; the deviation of around 13 % is agreeable. Finally, the curve calculated by Lassmann gives solubility values largely lower than the values calculated in our study; significant positive deviations are observed over the whole range of temperature.[4]

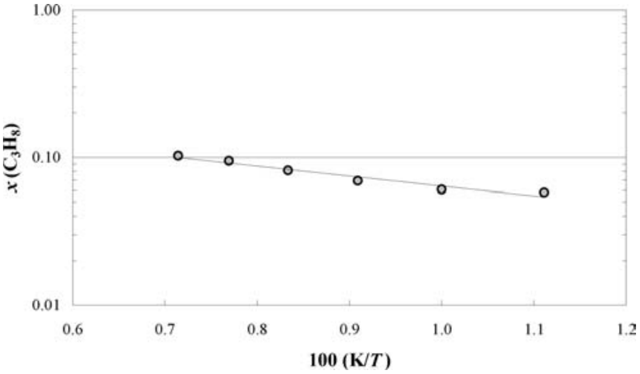

Figure 4. Calculated values of propane solubility $x(C_3H_8)$ in the oxygen-rich liquid phase for $T = (90 \text{ to } 140)$ K based on the PR EoS, the MHV2 mixing rule, and the NRTL activity coefficient model with adjusted binary interaction parameters from Table 3 as a function of T^{-1}.

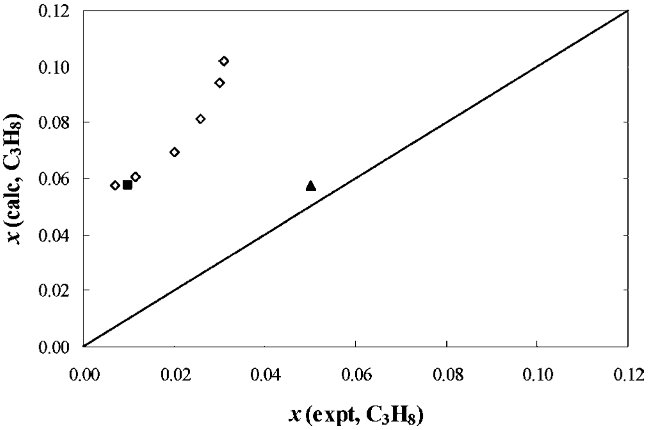

Figure 5. Calculated solubility of propane, $x(\text{calc}, C_3H_8)$, as a function of the measured solubility in the oxygen-rich liquid phase, $x(\text{expt}, C_3H_8)$, for $T = (90 \text{ to } 140)$ K: ■, Karwat experimental value;[2] ▲, McKinley and Wang experimental value;[3] ◇, Lassmann calculated values.[4]

As for the McKinley and Himmelberger value published in 1957,[1] except for the authors' error in temperature measurement, it is probably a liquid−solid solubility limit since the melting temperature of pure propane is 85.47 K.

Finally, on the basis of solubility values of propane in liquid nitrogen that are now available in the scientific literature, comparison with the data for the propane-lean liquid phase shows that the solubility of propane in liquid oxygen is higher than that in liquid nitrogen.[6,14]

Conclusions

(P, x) VLE data were experimentally determined for the oxygen + propane system at temperatures of (110.22, 120.13, 130.58, and 139.95) K with a device developed by CEP/TEP Laboratory allowing the accurate study of potentially flammable mixtures under safe conditions.

Thermodynamic modeling with adjusted parameters was employed to calculate the complete phase diagram for this binary system for temperatures below 154.58 K, the critical point of pure oxygen. A vapor−liquid−liquid equilibrium was highlighted by the modeling based on our experimental data. This particular thermodynamic behavior, which has been observed previously by several authors for the nitrogen + propane binary system, was confirmed by additional experiments allowing visualization of the physical phenomenon of demixing of liquid phases at atmospheric pressure and corresponding cryogenic temperature.

Furthermore, on the basis of this work, the solubility of propane in liquid oxygen can be determined for different cryogenic temperatures in both the propane-lean and propane-rich liquid phases. The calculated mole fraction solubility of propane in the oxygen-rich liquid phase is between 0.0693 and 0.1021 for temperatures from (110 to 140) K. A simple correlation to extrapolate solubility values to a temperature of 90 K has been proposed.

By extrapolation of our model for the oxygen + propane system, a satisfying agreement between our value of the solubility of propane in the oxygen-rich liquid phase at $T = 90$ K and the value of McKinley and Wang was observed. The other solubility values for the oxygen + propane system available in the scientific literature are greatly underestimated in comparison with the results of this work. The lack of data in the literature on this potentially flammable mixture has prevented us from making a complete comparative study.

Acknowledgment

The authors acknowledge A. Valtz, P. Théveneau, and the CEP/TEP Workshop (D. Marques and H. Legendre) for their help with technical and experimental aspects.

Literature Cited

(1) McKinley, C.; Himmelberger, F. The Role of Air Contaminants in Formulating Oxygen Plant Safety Principles. *Chem. Eng. Prog.* **1957**, *53*, 112–120.
(2) Karwat, E. Some Aspects of Hydrocarbons in Air Separation Plants. *Chem. Eng. Prog.* **1958**, *54*, 96–101.
(3) McKinley, C.; Wang, E. S. J. Hydrocarbon−Oxygen Systems Solubility. *Adv. Cryog. Prog.* **1960**, *53*, 11–25.
(4) Lassmann, E. Enrichment of Hydrocarbons in Pressurized Liquid Oxygen Evaporators. In *Safety and Reliability of Industrial Gases, Equipment and Facilities Seminar*; Compressed Gas Association: Houston, TX, 1995.
(5) van Konynenburg, P. H.; Scott, R. L. Critical Lines and Phase Equilibria in Binary van der Waals Mixtures. *Philos. Trans. R. Soc. London, Ser. A* **1980**, *298*, 495–594.
(6) Houssin-Agbomson, D.; Coquelet, C.; Richon, D.; Arpentinier, P. Equipment Using a "Static-Analytic" Method for Solubility Measurements in Potentially Hazardous Binary Mixtures under Cryogenic Temperatures. *Cryogenics* **2010**, *50*, 248–256.
(7) Guilbot, P.; Valtz, A.; Legendre, H.; Richon, D. Rapid On-Line Sampler-Injector. A Reliable Tool for HT−HP Sampling and On-Line Analysis. *Analusis* **2000**, *28*, 426–431.
(8) Laugier, S.; Richon, D. New Apparatus To Perform Fast Determinations of Mixture Vapor−Liquid Equilibria up to 10 MPa and 423 K. *Rev. Sci. Instrum.* **1986**, *57*, 469–472.
(9) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Sci.* **1976**, *15*, 59–64.
(10) Mathias, P. M.; Copeman, T. W. Extension of the Peng−Robinson Equation of State to Complex Mixtures: Evaluation of the Various Forms of the Local Composition Concept. *Fluid Phase Equilib.* **1983**, *13*, 91–108.
(11) Huron, M. J.; Vidal, J. New Mixing Rules in Simple Equations of State for Representing Vapour−Liquid Equilibria of Strongly Non Ideal Mixtures. *Fluid Phase Equilib.* **1979**, *3*, 255–271.
(12) Dahl, S.; Michelsen, M. L. High Pressure Vapour−Liquid Equilibrium with a Unifac-Based Equation of State. *AIChE J.* **1990**, *36*, 1829–1836.
(13) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Function for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.
(14) Szczepaniec-Cieciak, E.; Kondaurov, V. A.; Melikova, S. M. Study on the Solubility of Light Alkanes in Liquid Nitrogen. *Cryogenics* **1980**, *20*, 48–51.

Received for review May 28, 2010. Accepted July 27, 2010. The authors thank Air Liquide for financial support.

JE100574Y