Vapour-liquid Equilibrium Data for C5 Saturated-Unsaturated Hydrocarbons Solutions with Solvents Monopropylene Glycol, Dipropylene Glycol or *N*-Methyl-2-Pyrrolidone

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The influence of monopropylene glycol (MPG), dipropylene glycol (DPG), or N-methyl-2 pyrrolidone (NMP) solvents on the relative volatility of C5 alkanes in mixtures with C5 olefins was estimated based on vapour-liquid equilibrium data determined experimentally. An Othmer type equilibrium apparatus was used and compositions of phases were established by gas chromatography. The solvents capacity for saturated – unsaturated hydrocarbons separation by extractive distillation is quantified by the relative volatility α_m values, which were calculated from the experimental results. The two key parameters, R_{min} and N_{min} (minimum reflux ratio and minimum number of theoretical trays), for the design of a distillation column aimed to separate C5 alkenes from a refinery C5 cut, were consequently computed for three scenarios of bottom product quality. Values of R_{min} and N_{min} thus estimated proved the capability of the three tested solvents for C5 olefins separation by extractive distillation, their separation capacity increasing in the order : MPG<DPG<NMP.

Keywords: C5 fraction, vapour-liquid equilibrium, Othmer, extractive distillation

Value of C5 olefins as raw material in petrochemical industry rose constantly in recent years, grow which was particularly determined by their use in the manufacture of TAME (*tert*-amyl methyl ether) and TAEE (*tert*-amyl ethyl ether) employed as high octane components for the reformulated gasoline pool [1-3]. However, separation of C5 olefins (amylenes) from the refinery C5 cut, or alternatively, concentration of amylenes in the C5 refinery streams by traditional distillation, is difficult or even impossible due to close or overlapping boiling points of C5 alkanes and alkenes (table 1 for boiling points of several C5's).

In the practice of distillation towers design, the relative volatility, α, is commonly used to measure the separability of components from a binary mixture by distillation. When α is lower than a threshold value of about 1.05, like for several C5 alkanes and alkenes, the exceeding number of trays and reflux ratio needed for a given separation are leading to investment and separation costs prohibitively high. A technical solution which can be deemed in such a case is the extractive distillation, which is also adopted for C4 alkanes/alkenes separation [4, 5].

In the extractive distillation process an intendedly added particular solvent (also called dissolvent or extractive distillation agent) has the aim to enhance the relative volatilities. Beside rescaling of volatilities, the chosen solvent may lead to a complete reordering of component volatilities, depending on component-solvent inter-molecular interactions and thus to components' ordering on the volatility scale according to their affiliations to the various classes of compounds.

Three solvents were envisaged in our work for tests on their ability to improve C5 alkenes/C5 alkanes separation : 1,2-propandiol (commonly monopropylene glycol, MPG), dipropylene glycol (DPG), and *N*-methyl-2-pyrrolidone (NMP). NMP is a solvent with an already recognized utilization in petrochemical industry, in processes like liquid liquid extraction and extractive distillation. Specifically, the latter process is currently employed for the separation of C4 alkenes or butadiene from C4 cuts [4]. The choice of the other two solvents, MPG and DPG, was determined not only by their ability for the enhancement of relative volatility as predicted by thermodynamic modeling using Pro/II [6], but also by their price, low toxicity to humans and environment and their availability as by products on the autochthonous market.

To the best of our knowledge, the use of MPG and DPG solvents in extractive distillation of C5 cut has never been tested prior to our work. In addition, vapor-liquid equilibrium (VLE) data available in literature for C5 NMP mixtures are referring only to some members of the C5 hydrocarbons family [7 - 9]. In the latter reference, [9], predictive results using UNIFAC model are also given. Consequently, we have carried out experimental determinations of VLE data for C5 fraction in mixtures with the three mentioned solvents, MPG, DPG and NMP and the results are presented herein. A C5 fraction originating from a typical refinery stream containing both saturated and unsaturated C5 hydrocarbons was the starting material for the measurements, in order to effectively ascertain the feasibility of the C5 alkenes separation by extractive distillation.

Some preliminary results for limited range of concentrations have been presented in [10] for MPG and in [11] for DPG. Subsequently, these preliminary experimental data were compared with predictive VLE data computed with Pro/II package [6] using UNIFAC model (Lingby Dortmund version).

Experimental part

Materials

The initial raw C5 fraction was sampled from a refinery-representative C5 stream containing amylenes. Its average composition is given in table 1 (3rd column). The refinery

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C5 raw cut was first concentrated by fractionation on a lab column, collecting the fraction distilled between 34 and 40°C. This preconditioning fractionation was carried out with an equipment and conditions according to ASTM D 2892 distillation (also commonly named TBP, True Boiling Point, distillation) [12], that is with a 15 theoretical plates column and a 5/1 reflux ratio. The 34 - 40 °C C5 fraction was the starting feedstock used for the subsequent VLE experimental measurements. It was thus possible to have at our disposal a C5 fraction with a relatively high concentration, 81.12 % (mass), of C5 unsaturated hydrocarbons. However, it was possible to attain such a high content of amylenes in a C5 fraction as that given in table 1 (col. 4) by a conventional fractionation only with penalty on amylenes yield, since 3 methyl-1 butene and most of 1-pentene and 2-methyl-1-butene from the raw C5 cut were inherently discarded with the easier product (according boiling points in table 1).

First experimental VLE determination was carried out with the 34 - 40 °C C5 fraction, of highest concentration of unsaturated hydrocarbons (81.12%). A series of C5 fraction samples were subsequently prepared by dilution of the starting feedstock (the 34 - 40 °C fraction) with pure (analytical grade) *n* pentane in different proportions, in order to be able to cover a larger domain of concentrations of saturated hydrocarbons in the VLE measurements. Components concentrations in the C5 samples thus obtained were checked by gas chromatography (GC).

Monopropylene glycol (1,2-propandiol, MPG) solvent was purified by distillation in a lab Fisher glass column. Boiling point measured for MPG thus purified was differing by no more than ± 0.4°C the value reported in literature (187.6 °C [13]). DPG (dipropylene glycol) from Oltchim S. A., with a total dipropylene glycols content of 98%, was used as provided, impurities being water and TPG (tripropylene glycols, *i.e.* trimers of MPG). Commercial DPG is a mixture of three isomers of MPG dimers : 4-oxa-2,6 heptanediol or 1-(2-hydroxy-propoxy)-2-propanol, 2-(2-hydroxy-propoxy)-1-propanol and 2-(2-hydroxy-1-methyl-ethoxy)-1-propanol. Finally, NMP (*N*-methyl-2 pyrrolidinone) solvent (99%) from Merck was used as received.

The solutions C5 fraction samples – solvent were prepared with the following solvents concentrations : 95% MPG, 90 and 95% DPG, and 85, 90, 95% (mass) NMP. Mixtures with lower solvent contents have not been used for VLE determinations, because C5 hydrocarbons are no more completely soluble in the solvents. Thus, occurrence of two liquid phases was noticed for lower solvents ratios even at boiling temperatures. Study of vapor - liquid equilibrium for such systems with two liquid phases was anyway beyond the aim of the current stage of our work.

Equipment and procedure

The vapour and liquid phases at equilibrium were produced and collected separately using an Othmer apparatus made of glass (fig. 1). The flask 1 was placed inside a thermostat with temperature control.

The vapour-liquid equilibrium (VLE) was assumed achieved after 2 h of boiling with reflux and recirculation of liquid, with constant temperatures at thermometers 6 and 7. Cooling agent at -25°C was used for the vertical condenser 2. All VLE determinations have been carried out at atmospheric pressure.

Aliquots of 2 cm^3 were then withdrawn from both higher temperature boiling liquid in vessel 1 and condensate resulted from the vapor phase and collected in vessel 3. The compositions of aliquots have been determined by gas chromatography. For experiments carried out in presence of solvents, GC analysis were made only for aliquots from collector vessel 3, while the composition of

Table 1
COMPOSITION OF C5 FRACTIONS AND BOILING POINTS OF SEVERAL C5 HYDROCARBONS

Component	Normal boiling point [13], °C	Raw refinery C5 cut % mass (*)	Starting C5 fraction, % mass (**)
C4 hydrocarbons	- - -	1.88	- - -
isopentan	27.85	45.76	5.40
1-pentene (α-amylene)	29.97	5.37	4.45
n-pentane	36.07	8.36	13.48
isoprene	34.07	0.25	0.30
2-pentene (β-amylene)	36.07 (trans) ; 36.94 (cis)	12.58	34.35
piperylenes	42.0 (trans) ; 44.0 (cis)	0.65	0.29
isoamylenes	31.16 (2-methyl-1-butene) ;	7.26	3.99
	38.57 (2-methyl-2-butene) ;	12.06	36.91
	20.1 (3-methyl-1-butene)	1.34	- - -
cyclopentene	44.24	2.33	0.83
other and C5+ hydrocarbons	- - -	2.16	- - -
Specific weight (d_{15}^{15})	- - -	0.652	- - -

(*) content of C5 alkanes (*i*- and *n*-C_5H_{12}) 54.12 %, corresponding to 0.5342 molar fraction ;
(**) the starting C5 fraction undertaken in experimental VLE measurements (81.12 % mass total content of C5 alkenes), obtained in lab by cutting between 34 and 40 °C the raw C5 fraction sampled from refinery.

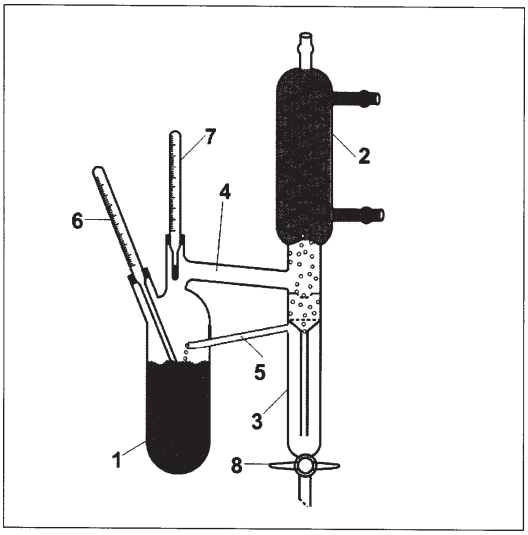

Fig. 1. Othmer apparatus with recirculation used for VLE measurements :
1 –flask; 2 – vertical condenser;
3 – cylindrical collector ;
4, 5 – connection tubes; 6, 7 – thermometers;
8 – tap

solvent-containing phase in distillation flask 1 was established by difference, from mass balances on hydrocarbons.

The gas-chromatograph was a HP 5890 Series II apparatus, with a configuration and operating parameters similar to those for PONA analysis (ASTM D 6293-98) [14]. Commercially available standard (Agilent) for refinery gas analysis was employed for calibration of both hydrocarbons retention times and concentrations.

Results and discussion

Considering the altered volatilities in the presence of solvents as aforementioned (see Introduction), the hydrocarbons of the C5 fraction are lumped into a binary mixture, with the saturated hydrocarbons being assumed the more volatile component and the olefins the heavier one. The herein presented experimental VLE data were obtained in order to quantify the capacity of the selected solvents to improve volatility of C5 saturated hydrocarbons relative to the volatility of C5 alkenes. Consequently, the main task of the experimental work was to determine saturated/unsaturated hydrocarbons relative volatility values, in order to finally ascertain the solvents potential for an efficient C5 alkenes separation by extractive distillation.

Table 2

MEASURED DATA FOR VAPOR-LIQUID EQUILIBRIUM (VLE) OF C5 FRACTION (C5 SATURATED HYDROCARBONS ASSUMED THE MORE VOLATILE COMPONENT)

x, mole fraction (liquid phase)	*y*, mole fraction (vapor phase)
0.1838	0.1898
0.1940	0.2020
0.2742	0.2952
0.3021	0.3205
0.3936	0.4181
0.3983	0.4188
0.7435	0.7483
0.7461	0.7541
0.7457	0.7546
0.7443	0.7527

The experimental results obtained for C5 fraction without solvent are given in table 2.

The results obtained from VLE measurements with mixtures of C5 fractions and the solvents MPG, DPG, NMP are shown in table 3. All data in table 3 are reported on a base without solvent.

The relative volatility values are computed using experimental x_i and corresponding y_i molar fractions values given in tables 2 or 3 and equation (1) :

$$\alpha_i = \frac{\frac{y_i}{1-y_i}}{\frac{x_i}{1-x_i}} \quad (1)$$

An average value for the relative volatility, α_m , was also established as an arithmetic mean of the relative volatilities α_i previously computed. The average relativity volatilities, α_m , thus found for both C5 fraction with and without solvent are given in table 4 (col. 2).

A quantitative estimation of the efficiency, cost and energy demand for the separation between saturated C5 and unsaturated C5 hydrocarbons may be provided by the values of parameters R_{min}, the minimum reflux ratio, and N_{min}, the minimum numbers of trays [15, 16], needed to achieve the required purity of distillation, top and bottom, products. R_{min} was computed with relation (2):

$$R_{\min} = \frac{x_d - y_f}{y_f - x_f} \quad (2)$$

according to Underwood's method [15, 17], where x_f represents the molar fraction of the easier component (C5 saturated hydrocarbons in our case) in the initial C5 raw cut when in liquid phase and at bubble point (*i.e.* with thermal condition = 1, [5, 17]). Being more specific, x_f = 0.5342 , as previously indicated for our raw C5 cut sampled from refinery (first note below table 1) ; y_f is the molar fraction of the easier component (C5 saturated hydrocarbons) in vapour phase at equilibrium with the liquid phase of x_f concentration. Molar fractions y_f were then calculated with :

$$y_f = \frac{\alpha_m \cdot x_f}{1 + (\alpha_m - 1) \cdot x_f} \quad (3)$$

equation which can be readily derived from (1) (also given in [5, 15 or 17).

Same values (within drawing errors) for y_f may be obtained if read from the *x - y* equilibrium curves plotted with experimental points (x_{iexp} , y_{iexp}). The values of molar fractions y_f computed with relation (3) are given in table 4.

Based on literature [15, 16] referring to the purity commonly imposed to the top product of the distillation column, a value of 0.9 was assigned to x_d (x_d = 0.9, mole fraction of C5 alkanes in top product), and used in equation (2) for the estimation of R_{min} .

Table 3

VLE DATA MEASURED FOR SYSTEMS SATURATED C5 HYDROCARBONS - C5 ALKENES - SOLVENT (MOLE FRACTIONS ON A BASE WITHOUT SOLVENT ; C5 SATURATED HYDROCARBONS ASSUMED THE MORE VOLATILE COMPONENT)

Solvent to C5 fraction weight ratio	*x*, mole fraction	*y*, mole fraction
MPG 95/5	0.1548	0.2120
	0.3801	0.5053
	0.5262	0.6356
	0.7135	0.7841
DPG 90/10	0.1701	0.2095
	0.4912	0.6221
	0.6621	0.7453
	0.7311	0.8031
DPG 95/5	0.1581	0.2230
	0.3682	0.5012
	0.5306	0.6821
	0.7638	0.8421
NMP 85/15	0.1701	0.2095
	0.4902	0.6103
	0.6612	0.7453
	0.7301	0.7902
NMP 90/10	0.1582	0.2331
	0.3681	0.5221
	0.5307	0.7020
	0.7639	0.8521
NMP 95/5	0.1548	0.2520
	0.3803	0.5515
	0.5261	0.7221
	0.7513	0.8563

Table 4
RELATIVE VOLATILITIES (AVERAGE, α_m), MINIMUM REFLUX RATIOS (R_{min}) AND MINIMUM NUMBERS OF THEORETICAL TRAYS (N_{min}) DETERMINED FOR THE STUDIED SYSTEMS

Solvent / C5 fraction (mass ratio)	α_m	x_b	y_f	R_{min}	N_{min}
0	1.04	0.10	0.5439	36.54	111.04
		0.20			90.37
		0.30			76.63
MPG 95/5	1.78	0.10	0.6712	1.67	6.62
		0.20			5.21
		0.30			4.28
DPG 90/10	1.71	0.10	0.6623	1.86	7.19
		0.20			5.68
		0.30			4.67
DPG 95/5	1.88	0.10	0.6831	1.46	5.96
		0.20			4.68
		0.30			3.82
NMP 85/15	1.63	0.10	0.6515	2.12	7.99
		0.20			6.33
		0.30			5.23
NMP 90/10	1.88	0.10	0.6831	1.46	5.96
		0.20			4.68
		0.30			3.82
NMP 95/5	2.07	0.10	0.7036	1.16	5.04
		0.20			3.93
		0.30			3.18

The minimum numbers of trays, N_{min}, are determined with Fenske-Underwood equation (4):

$$N_{\min} = \frac{\lg \frac{x_d}{1-x_d} - \lg \frac{x_b}{1-x_b}}{\lg \alpha_m} - 1 \qquad (4)$$

where x_b is the molar fraction of C5 saturated hydrocarbons in the bottom product [15, 17]. Values of x_b were chosen 0.1, 0.2 or 0.3, according to three scenarios for the purity of the desired product.

Because the relative volatility is low, 1.04 , in the absence of the solvent, both R_{min} and N_{min} show huge values, that is around 37 and between 76 and 111, respectively, for all the three separation scenarios. Such high values show that separation between C5 alkenes and C5 alkanes by a simple distillation is for sure impractical. Always from the data in table 4, we can notice soared relative volatilities in the presence of solvents, amongst which the most important rises are observed for DPG and NMP. Thus, value of α_m is almost doubled, up to 2.07, in the case of the latter solvent, while for DPG the average relative volatility is 1.64 or 1.8 times higher for solvent ratio 90/10 or 95/5 than the relative volatility in the absence of solvent (fig. 2).

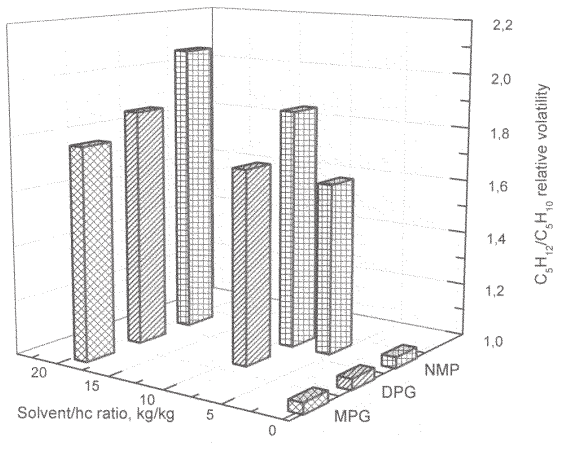

Fig. 2. C5 saturated hydrocarbons / C5 olefins relative volatilities (α_m) determined for various ratios of solvent (MPG, DPG or NMP) to hydrocarbons (for comparison, α_m = 1.04, found for no solvent case, is also represented at solvent/C5 fraction = 0)

Consequently, R_{min} and N_{min} values computed from VLE in the presence of solvents are significantly lower than those determined from VLE in the absence of solvents. For example, a decrease of R_{min} by more than 21 times and of N_{min} by 16 to 18 times may be observed when MPG solvent is used at a 95/5 ratio. Correspondingly, DPG leads to values of R_{min} 21.8 times smaller and of N_{min} 18.7 to 20 times lower than in the absence of the solvent. When a 90/10 DPG ratio is used, same parameters are again considerably decreased, *i.e.* 15.6 and 15.4 to 16.4 times smaller, respectively, then without-solvent distillation. In agreement with the most pronounced enhancement of the relative volatility, NMP solvent shows the steepest diminutions of R_{min} and N_{min} . Thus, for the highest NMP ratio used (95/5), R_{min} and N_{min} drop to values 23 times and 22 to 24 times lower, respectively, than those found from no-solvent determinations. For the other two NMP ratios tested, the two parameters are again remarkably decreased, for example 20 times and 18.6 to 20 times in the case of the intermediary ratio (9/1).

Conclusions

Using an Othmer apparatus, new VLE data have been obtained for mixtures containing C5 alkanes – C5 alkenes and one of the solvents MPG, DPG and NMP. Assuming the former hydrocarbons of C5 fraction lumped into the volatile component and the latter ones into the heavier component, average values of the relative volatility, α_m, are computed based on experimental *x* - *y* VLE data. Strong enhancement of α_m is observed for all three solvents and the entire range of solvent ratios tested, the increasing effect being in the order : MPG < DPG < NMP. From a value of α_m as low as 1.04 in the absence of solvent, soared values of the relative volatilities, up to 1.88 for DPG or 2.07 for NMP, are thus determined. Values of N_{min} , the minimum number of trays, and of R_{min}, minimum reflux ratio, two key

parameters in the design of a distillation column, are also computed for three purities imposed on the desired product, the C5 alkenes in column bottom. It is consequently observed that the use of solvents led to values of N_{min} and R_{min} by 15 to more than 20 times lower when compared to the values found for without-solvent case. It is thus proved that all three selected solvents can decisively improve the separation efficiency of alkenes from a refinery C5 cut, with NMP being the most beneficial.

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Legend

N – number of trays
R – reflux ratio
x – mole fraction (volatile component, liquid phase)
y – mole fraction (volatile component, vapor phase)
α – relative volatility

Subscripts

b – bottom product
d – distillate (top) product
f – feed
i – number of points (on *x-y* VLE curve)
m – average
min – minimum

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y – mole fraction (volatile component, vapor phase)
a – relative volatility

Subscripts
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d – distillate (top) product
f – feed
i – number of points (on x y VLE curve)
m – average
min – minimum

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