

The Influence of Di-Propylene-Glycol on the Liquid Vapor Equilibrium in the C₅ Saturated – Isoamilenes System

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Abstract

In order to improve the separation of saturated hydrocarbons from unsaturated hydrocarbons in the pentanic C₅ fraction, there has been performed liquid – vapor equilibrium experimental determinations for the isoamilene – nC₅ unsaturated hydrocarbons and iC₅ saturated hydrocarbons in the presence of di-propylene-glycol. The experimental results are presented under the form of y – x system equilibrium diagrams on base without solvent.

Key words: liquid – vapor equilibrium, equilibrium diagrams, isoamilene, solvent.

Introduction

One of the possibilities of increasing the relative volatility level is that which represents the basis of the extractive fractioning process, which means, adding a lesser volatile substance to the mixture that needs to be separated, a substance named solvent, dissolvent or extractive distillation agent, in the presence of which non-ideal behavior is created, or modifies the existing non-ideal behavior, thing which finally leads to the increase of the relative volatility level.

In the case of liquid phase non-ideal behavior binary mixtures, the relative volatility α' can be defined with the help of the relation (1).

$$\alpha' = \frac{P_1}{P_2} \cdot \frac{\gamma_1}{\gamma_2} \quad (1)$$

Where: $\frac{P_1}{P_2}$ and $\frac{\gamma_1}{\gamma_2}$ represent the vapor pressures ratio, respectively the ratio of the activity coefficients of the two components among which the separation process takes place.

In order to increase the relative volatility α' , the solvent must act differently as compared to the other two components of the mixture. This feature, of the solvent's behaving differently, in the sense of a faster increase rate of γ_1 compared to γ_2 , is named: selectivity. So, the essential

characteristic of the solvent in favor of an easy separation is selectivity, feature that needs to be as high as possible throughout the entire concentration domain of the mixture.

In the case further presented, I have analyzed a pentanic fraction which has been considered a hypothetic binary, the alkanes being the more volatile component, and the lesser volatile component being the alkenes. In view of optimizing this process of separation, experiments have been performed regarding the influence of the di-propylene glycol solvent $C_6H_{14}O_3$ (DPG) on the relative volatility of the isoamilene – C_5 saturated hydrocarbons hypothetic binary.

Experimental work

The liquid – vapor equilibrium data has been determined for the same pentanic fraction, in the presence of DPG.

The experimental data has been recorded with the help of an OTHMER type apparatus, built and adapted for the parameters of the extractive distillation and which is presented in figure 1.

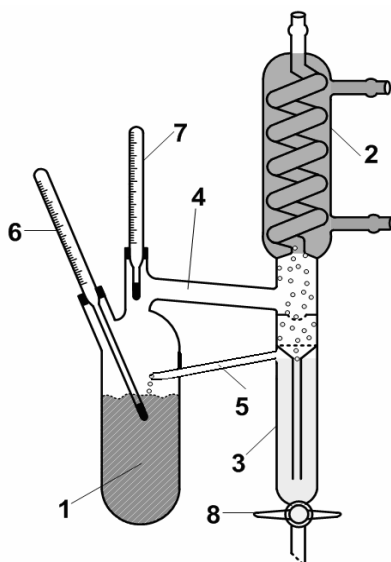


Fig. 1. The “OTHMER type” equilibrium apparatus which deals with the recirculation of condensed vapors.

Apparatus description

The equilibrium device shown in figure 1, is formed of a distillation vessel (1), an ascendant condenser (2), an accumulation tank, destined for the distilled product, the connectors (4) and (5), two thermometers, (6) and (7) for measuring the liquid and vapor temperature, a faucet (8) necessary for testing samples from the accumulation tank.

Because the accumulation tank is linked with the atmosphere through the vertical condenser, the equilibrium determinations are calculated at atmosphere pressure.

In order to obtain a $x - y$ equilibrium point, we must pass through the following stages:

- a mixture quantity is introduced in the distillation apparatus
- the faucet and the thermometers are connected to the apparatus
- the cooling water is turned on

- the heating system of the distillation tank is connected to the electric network with the help of an autotransformer.

This new solvent, has been used in two different concentrations in mixture with the pentanic fraction, expressing the concentrations at the equilibrium x' and y' being made “on base without solvent”.

When graphically representing they – x equilibrium curves, the mixture was considered to be a saturated hydrocarbons – unsaturated hydrocarbons, on base “without solvent”, the saturated hydrocarbons being the more volatile component, whereas the unsaturated hydrocarbons being the lesser volatile component.

In the following stages, from the experimental results, there has been a solvent with a 90% concentration and 95%, and there have been obtained the following $y - x$ equilibrium curves, presented in figure 2.

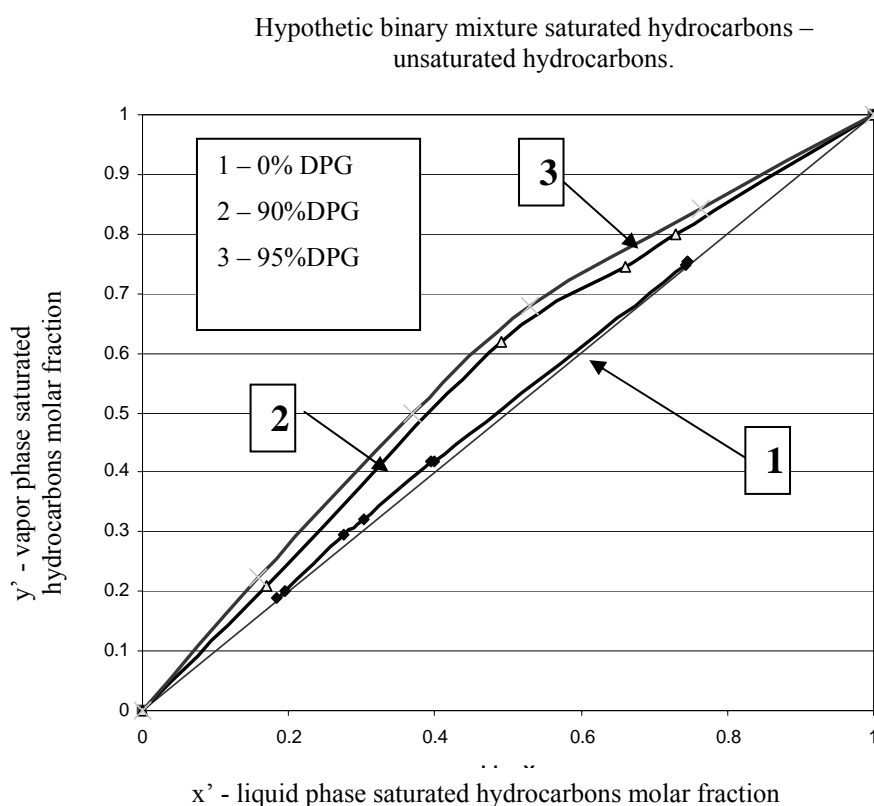


Fig.2 The influence of the solvent’s (DPG) concentration on the liquid - vapor equilibrium curve, in the y' and x' coordinates, of the isoamilenes – C_5 saturated hydrocarbons hypothetic binary mixture, where y' and x' represent the molar fractions of the more volatile component in vapor, respectively in liquid, after the total removal of the solvent, respectively, the concentrations of the phases at the point of equilibrium, on base “without solvent”.

Results and discussions

From the analysis of these curves, the conclusion resides in a higher value of the concentration of the vapor phase saturated hydrocarbons as compared to their liquid phase, for the experiment performed in the presence of the solvent.

For the hypothetical binary, saturated hydrocarbons – unsaturated hydrocarbons in the presence of a 90% concentration and 95% mass DPG solvent, the α_m' average relative volatility, was calculated with the help of the relation (2).

$$\alpha_m' = \frac{\frac{y_m'}{1 - y_m'}}{\frac{x_m'}{1 - x_m'}} \quad (2)$$

Where:

- y_m' - the molar fraction of the more volatile component in gaseous phase;
- x_m' - the molar fraction of the more volatile component in liquid phase;
- α_m' - the volatility of the component with a boiling point lower, as compared to the component with a higher boiling point for $x_m'=0,5$ in the presence of the solvent.

Table 1. The average relative volatility α_m' for the unsaturated hydrocarbons - saturated hydrocarbons hypothetical binary mixture in the presence of a 90% concentration and 95% mass DPG.

Unsaturated hydrocarbons – saturated hydrocarbons hypothetical binary mixture dissolvent	
solvent	α_m' for $x=0,5$
Without solvent	1,04
DPG 90%masss	1,71
DPG 95% masss	1,88

For equilibrium curve number 2 from figure 2 $x_m'=0.5$ and $y_m'=0.6310$, the average relative volatility being $\alpha_m'=1.71$ in the case of 90% mass solvent in the mixture, and for equilibrium curve number 3 from figure 2, $x_m'=0.5$, and $y_m'=0.6528$, $\alpha_m'=1.88$ for 95% mass solvent in the mixture.

The quantitative observation regarding the influence on the separation of isoamilenes from C_5 saturated hydrocarbons is made through the minimum reflux ratio (R_{min}) and through the minimum number of trays (N_{min}).

Regarding R_{min} it can be calculated with the help of the following relation

$$R_{min} = \frac{x_d - y_f}{y_f - x_f} \quad (3)$$

Where:

- x_d – represents the C_5 saturated hydrocarbons molar fraction in the highest purity product.
- x_f - the C_5 saturated hydrocarbons molar fraction in liquid phase of the feed flux
- y_f - the C_5 saturated hydrocarbons molar fraction in vapor phase of the feed flux (at equilibrium with the liquid phase which is of the x_f concentration)

The y_f concentration value is calculated with the help of the relation (4)

where α_m' represents the average relative volatility of the isoamilenes – C_5 hydrocarbons binary (on base without solvent), value that is calculated with the help of the relation (2).

Regarding the (N_{min}) minimum number of trays, it can be calculated with the help of Fenske's relation:

$$N_{\min} = \frac{\lg \frac{x_d}{1-x_d} - \lg \frac{x_b}{1-x_b}}{\lg \alpha_m} - 1 \quad (5)$$

Where x_b – represents the C₅ saturated hydrocarbons molar fraction in the product at the base of the fractioning column.

Using these relations, the (N_{min}, R_{min}) minimum parameters for the multiple variants taking into account the α_m average relative volatility, has been calculated. The results are presented in table 2. Taking into account the x_f, feed flux composition, values for x_d, x_b, have been imposed, thus observing the variation of the R_{min} and N_{min} parameters in the case of isoamilenes – C₅ saturated hydrocarbons hypothetic binary and in the presence of the (DPG) solvent. The obtained values are presented in table 2.

Table 2. The variation of R_{min} and N_{min} parameters in the case of separating the unsaturated hydrocarbons – saturated hydrocarbons hypothetic binary, without and in the presence of the solvent, for fixed values of the x_f, x_d, x_b parameters.

Solvent %	α	x _d	x _f	x _b	y _f	R _{min}	N _{min}
Without solvent	1.04	0.9	0.53	0.1	0.54	36.00	111.04
	1.04	0.9	0.53	0.2	0.54	36.00	90.37
	1.04	0.9	0.53	0.3	0.54	36.00	76.63
DPG 90%	1.71	0.9	0.53	0.1	0.64	2.36	7.19
	1.71	0.9	0.53	0.2	0.64	2.36	5.68
	1.71	0.9	0.53	0.3	0.64	2.36	4.67
DPG 95%	1.88	0.9	0.53	0.1	0.66	1.69	5.94
	1.88	0.9	0.53	0.2	0.66	1.69	4.68
	1.88	0.9	0.53	0.3	0.66	1.69	3.81

The obtained results show that N_{min} and R_{min} decrease approximately 15 times in the case “without solvent” as compared to its use at a 90% mass.

In the case of using a 95% mass solvent concentration as compared to the situation “without solvent”, the results show that N_{min} decreased approximately 18 times and R_{min} decreased approximately 19 times. In the case of increasing the solvent’s concentration from 90% mass to 95% mass, N_{min} decreases 1,2 times and R_{min} decreases approximately 1,3 times. For a better observation of R_{min} and N_{min} variations, I have provided the graphic from figure 3.

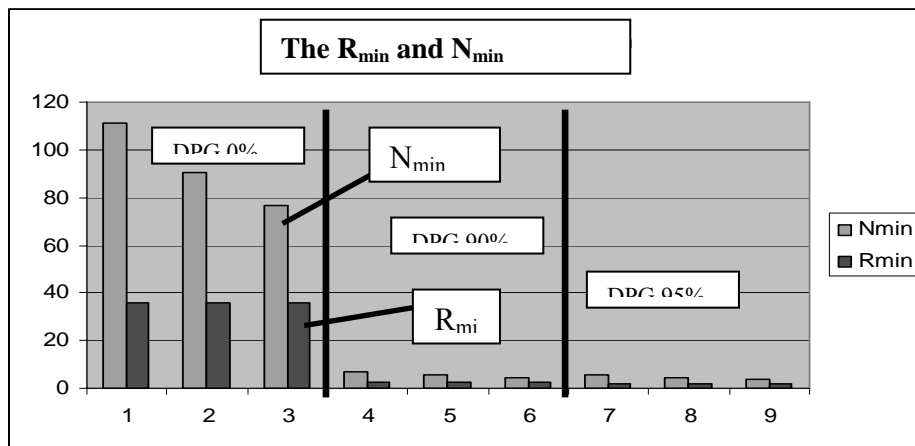


Fig. 3. The R_{min} and N_{min} variation in the case “without solvent”, parts 1,2,3; in the presence of a 90% mass solvent, parts 4,5,6; in the presence of a 95% mass solvent, parts 7,8,9.

Conclusions

For the experimental determinations of the previously considered binary equilibrium points, the “OTHMER type equilibrium apparatus that deals with condensed vapors recirculation”, presented in figure 1, has been used, apparatus built and calibrated in the laboratory to suit the conditions for extractive distillation.

In the case of $y - x$ equilibrium curves determined in the presence of a DPG, we can observe a substantial α' relative volatility increase, of the hypothetical hydrocarbon, respectively on base “without solvent”, for the 90% mass DPG in the system, comparing with the system without solvent the α' relative volatility is rising from 1,04 to 1,71 and for 95%mass solvent up to 1,88, which means a better separation .

The R_{\min} and N_{\min} calculated values clearly prove the substantial improvement of the separation process of saturated hydrocarbons from isoamilenes in the presence of the di-propylene-glycol, the R_{\min} is smaller in presence of DPG in the system this parameter decrease from 36 for the experiments without solvent to 2,36 for DPG 90% mass in to the mixture and to 1.69 for 95%mass DPG, for the same concentrations of feed, top, and base products. Also for the same concentrations of the products N_{\min} is decreasing form 111 to 3,81 in the presence of 95%mass DPG in the system

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Influența dipropilen glicolului asupra echilibrului lichid – vapori în sistemul izoamilene – hidrocarburi saturate C_5

Rezumat

Pentru îmbunătățirea separării hidrocarburilor saturate de hidrocarburi nesaturate din fracția pentanică C_5 , s-au efectuat determinări experimentale de echilibru lichid vapori pentru sistemul hidrocarburi saturate iC_5 și nC_5 – izoamilene în prezență de dipropilen glicol. Rezultatele experimentale sunt prezentate sub forma diagramelor de echilibru în sistem $y-x$ pe bază fără solvent