The Influence of the Molecular Interaction on the Solubility of Propylene and Propane in Different Solvents

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Abstract

This paper presents an experimental study regarding the solubility of propylene and propane in three solvents with multiple industrial applications: N-methylpirrolidone (NMP) and dimethylformamide (DMF), propyleneglycol (PG) at the temperatures of 293.15 K, 315.15 K and 333.15 K and pressure of 306-368 KPa. The solubility of propylene and propane depends not only on temperature and pressure, but also on the chemical nature of the solvent. In order to compare the experimental results and to show the effect of the solvent's nature, the solubility of the propylene and propane is expressed under the form of the molecular interaction parameter (mip). At the same temperature and pressures, the effect of the solvent's structure can be summarized as:

mip propylene in DMF > mip propylene in NMP > mip propylene in PG;
mip propane in NMP > mip propane in DMF > mip propane in PG

Key words: *propylene, propane solubility, solvents, molecular interaction parameter*

Introduction

Most of refinery gas fluxes contain in various proportions saturated and unsaturated hydrocarbons that must be recovered because they represent crude material, important components for the field of petrochemistry. Because of the high price of propylene, its recuperation is imposed from the mixture with propane and from mixtures with other components. Separating propylene from propane can be made through the classic distillation in columns with a large number of trays and high reflux ratios [1]. But, in the case in which propylene is in a mixture with inert gases, this process can not be utilized. Recently, was shown that the propylene removal at a lower purity than the one necessary for polymerization, a propylene that should be utilized in vapor phase for petrochemical purposes, can be obtained through a process of absorption at low pressures and (2…6 bar) in the presents of absorbents used as solvents in the process of extractive distillation: *N*-methylpirrolidone (*NMP*) and dimethylformamide (*DMF*) [2]. In order to simulate the absorption process it is necessary to know the solubility data of propylene and propane in the used solvents. These have been experimentally obtained at temperatures of 293.15, 313.15 and 333.15 K and pressures between 101.3 and over 607.8 kPa in *NMP* and *DMF* anhydrous and also in the presence of water [3, 4]. The present paper has as first purpose presenting new solubility data of propylene and propane and the propylene glycol (*PG*) solvent at temperatures of 293.15, 313.15 and 333.15 K and pressures between 308 and 327 kPa. The second purpose was to explain the influence of the

complex interactions between the gas solute and liquid solvent over the solubility of propylene-solvents pairs and propane-solvents pairs. It use the term "molecular interaction parameter" (*mip*) proposed by Hayduk and Wong [5].

Experimental

The experimental determination of propylene and propane solubility in *PG* has been made with a proper equilibrium apparatus. Details concerning the component parts of the apparatus, the operating mode and solubility data calculus are presented in previous papers [2, 3, 4].
Dimethylformamide, *N*-methylpirrolidone and propylene glycol are well-known solvents whose physical properties are presented in Table 1.

Table 1. Physical properties of the solvents [6]

Physical Properties	DMF	NMP	PG
Formula	C_3H_7NO	C_5H_9NO	$C_3H_8O_2$
Molecular weight, g/mol	73.09	99.13	76.09
Liquid density, g/cm^3,	0.944	1.028	1.036
Boling point	153 °C (426 K)	202 °C (475.15 K)	188.2 °C (461.35 K)
Viscosity, cP	0.92 at 20 °C	2.22 at 20 °C	55.32 at 20 °C
Dipole Moment, *D*	3.82 (25 °C)	4.09 (25°C)	3.60 (25 °C)
Dielectric Constant	36.7	32.2	No data
Solubility Parameter , cal/cc$^{0.5}$	12.1	11.2	14.46
Specific Gravity at 25°C	0.945	1.027	1.0413

The experimental results regarding the solubility of propylene and propane in *PG* anhydrous are presented in Table 2 and the results regarding *DMF* and *NMP* anhydrous, are presented in Tables 3 and 4.

Table 2. The solubility of propylene and propane in *PG* anhydrous

Temperature, K	Initial pressure, kPa	Final pressure, kPa	ΔP, kPa	$n = \dfrac{\Delta PV}{RT}$, moles	$x = \dfrac{n}{n + n_{absorbent}}$, molar fractions
Propylene					
293.15	469.02	312.61	157.02	0.0575	0.0365
313.15	446.73	320.61	126.12	0.0432	0.0283
333.15	443.69	331.45	112.44	0.0361	0.0244
Propane					
293.15	451.80	335.30	116.70	0.0426	0.0273
313.15	437.62	335.30	102.31	0.0350	0.0234
333.15	454.84	357.18	97.75	0.0314	0.0212

Table 3. The solubility of propylene and propane in *DMF* anhydrous

Temperature, K	Initial pressure, kPa	Final pressure, kPa	ΔP, kPa	$n = \dfrac{\Delta P V}{R T}$, moles	$x = \dfrac{n}{n + n_{absorbent}}$, molar fractions
Propylene					
293.15	871.24	362.91	508.32	0.1854	0.1250
313.15	621.98	357.59	264.39	0.0903	0.0661
333.15	463.35	319.10	144.25	0.0463	0.0360
Propane					
293.15	581.36	361.64	219.72	0.0801	0.0582
313.15	504.98	359.62	145.37	0.0496	0.0375
333.15	459.40	360.22	99.17	0.0318	0.0248

Table 4. The solubility of propylene and propane in *NMP* anhydrous

Temperature, K	Initial pressure, kPa	Final pressure, kPa	ΔP, kPa	$n = \dfrac{\Delta P V}{R T}$, moles	$x = \dfrac{n}{n + n_{absorbent}}$, molar fractions
Propylene					
293.15	566.27	321.12	245.15	0.0894	0.0798
313.15	603.04	349.49	185.68	0.0634	0.0482
333.15	480.67	368.33	112.34	0.0361	0.0349
Propane					
293.15	631.71	349.49	282.22	0.1105	0.0954
313.15	537.30	348.98	188.32	0.0687	0.0525
333.15	382.61	306.13	76.48	0.0245	0.0240

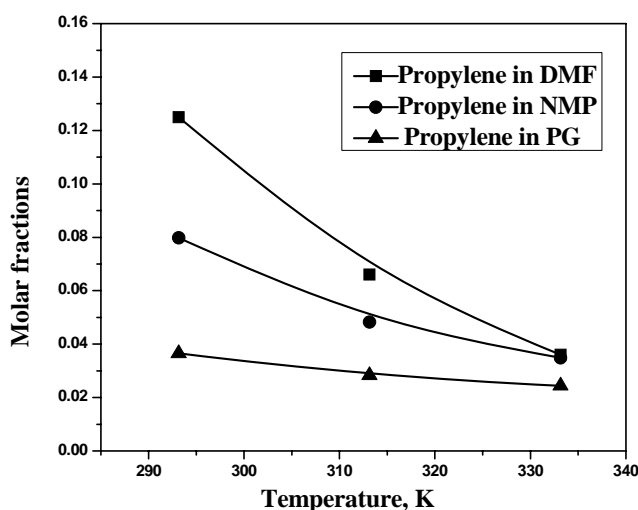The data from Tables 2, 3and 4 are graphically represented in Figures 1 and 2.

Fig 1. The influence of the temperature and the solvent nature over the propylene solubility
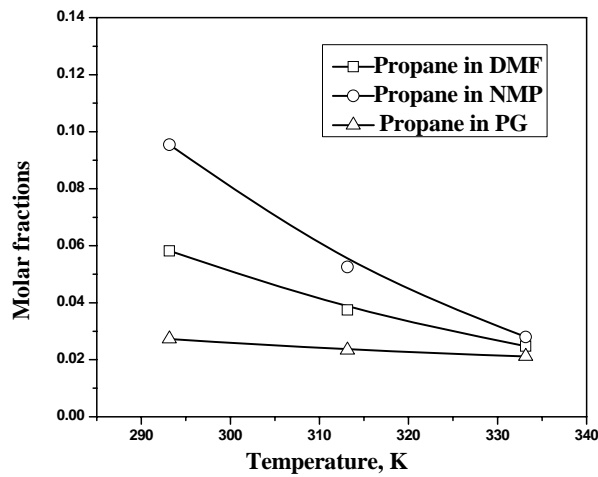
Fig 2. The influence of the temperature and the solvent nature over the propane solubility

Form the data presented in Tables 2, 3 and 4 and Figures 1 and 2 results that:
• independent by the nature of the solvent and solute, with the temperature increasing, the gases solubility decreases;
• at the temperature of 333 K, the propylene solubility is slowly dependent by the solvent nature and the propane solubility is very slow dependent by the nature of the solvent;
• at a constant temperature, the solubility of propylene decreases, in order: *DMF>NMP>PG*;
• at a constant temperature, the solubility of the propane decreases in order: *NMP>DMF>PG*.

Results

The solubility of gases in a certain solvent, depends on the nature of the solute (saturated or unsaturated), depends on the nature of the solvent (interactions between the molecules of the solvent) and also depend on the interactions between the molecules of the solute and solvent. Hayduk and Wong proposed, that these complex interactions between the pair solute-solvent, to be expressed with the help a term that they named "molecular interaction parameter" (*mip*) [5]. Calculating this parameter starts from well-known equations of the equilibrium liquid-vapor:

$$P \cdot y_S = P_S^t \cdot x_S \qquad (1)$$

where: P represents the equilibrium pressure (final pressure);

y_S, x_S - the molar fraction of the solute in vapor phase, respectively, in liquid phase;

P_S^t - the vapor pressure of the solute at equilibrium temperature.

Equation (1) represents the liquid-vapor equilibrium relation for binary systems with ideal behavior in both phases. From this equation, we have the result that the molar fraction of the solute in liquid phase with ideal behavior can be calculated as it follows:

$$x_S = \frac{P \cdot y_S}{P_S^t} \qquad (2)$$

But, in the presence of the solvent, the solute behavior in liquid phase is no ideal, so it means that the liquid-vapor equilibrium equation is shown by:

$$P \cdot y_S = P_S^t \cdot x'_S \cdot \gamma_S \tag{3}$$

where: x'_S represent the molar fraction of the solute in liquid phase with no ideal behavior;

γ_S - the activity coefficient of the solute.

From equation (3), we have the result that, the molar fraction of the solute in liquid phase with a no ideal behavior, can be calculated as it follows:

$$x'_S = \frac{P \cdot y_S}{P_S^t \cdot \gamma_S} \tag{4}$$

Dividing equation (4) by equation (2), we have the result that:

$$\frac{x'_S}{x_S} = \frac{1}{\gamma_S} = \alpha \tag{5}$$

In equation (5), α represents the molecular interaction parameter, and as it is shown, it represents the inversion of the activity coefficient of the solute in liquid phase, in the presence of solvent.

Continuing this study, for each solute-solvent pair, we have calculated, with equation (1), the molar fractions x_S, in the case of ideal behavior of the liquid phase. Because the studied solvents have a very low vapor pressure at the temperatures taken into account, we must consider that in vapor phase, only the solute is present, meaning $y_S = 1$.

Vapor pressures of the propylene and propane at temperatures of 293.15, 313.15 and 333.15 K, have been calculated by using Antoine's equation in which the coefficients A_i, B_i, C_i are presented in literature [7]. Regarding the molar fractions of propylene and propane in liquid phase with a no ideal behavior, x'_S, these represent, in fact, the solubility of each solute in the studied solvents and their values being obtained experimentally and previously presented in Tables 2, 3 and 4 and also the equilibrium pressures P which are the ones experimentally obtained. Results of the molecular interaction parameter calculations (*mip*), noted with the symbol α are presented in Table 5.

Table 5. Molecular interaction parameter (*mip*)

Solut-solvent pair:	Propylene-DMF			
Temperature, K	Equilibrium pressure P, kPa	x_S, molar fraction	x'_S, molar fraction	α
293.15	362.91	0.3741	0.1250	0.3341
313.15	357.59	0.2179	0.0661	0.3032
333.15	319.10	0.1290	0.0360	0.2789
Solut-solvent pair:	Propylene -NMP			
293.15	321.12	0.3137	0.0798	0.2543
313.15	349.49	0.2007	0.0482	0.2351
333.15	368.33	0.1491	0.0349	0.2340
Solut-solvent pair:	Propylene -PG			
293.15	312.61	0.3054	0.0365	0.1195
313.15	320.61	0.1954	0.0283	0.1448
333.15	331.45	0.1340	0.0244	0.1820
Solut-solvent pair:	Propane-DMF			
293.15	361.64	0.4289	0.0582	0.1356
313.15	359.62	0.2626	0.0375	0.1427
333.15	360.22	0.1725	0.0248	0.1437

Solut-solvent pair:	Propane-NMP			
293.15	349.49	0.4145	0.0954	0.2302
313.15	348.98	0.2548	0.0525	0.2059
333.15	306.13	0.1466	0.0240	0.1637
Solut-solvent pair:	Propane-PG			
293.15	335.30	0.3977	0.0273	0.0686
313.15	335.30	0.2448	0.0234	0.0955
333.15	357.18	0.1710	0.0212	0.1239

On account of the data presented in Table 5, we have graphically represented the variations of the interaction parameter of propylene with the three solvents, (Figure 3) respectively, of propane with the studied solvents (Figure 4), taking into account the temperature.
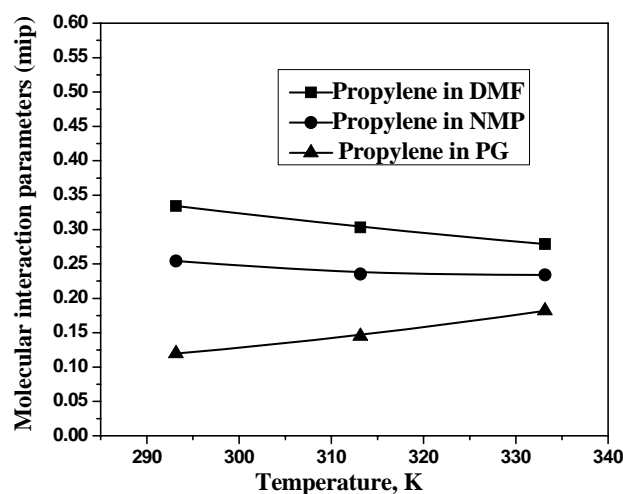

Fig 3. Variation of propylene interaction parameter in *DMF, NMP* and *PG* at different temperatures.
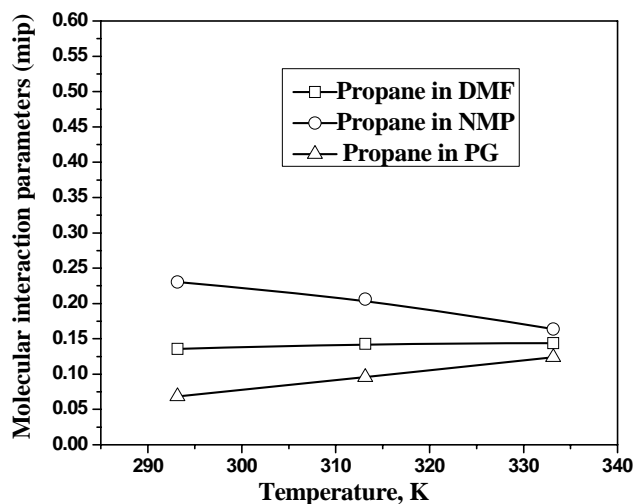

Fig 4. Variation of propane interaction parameter in *DMF, NMP* and *PG* at different temperatures.

The solubility of gases in solvents is a process that depends on a multitude of factors: temperature, pressure, the nature of the solvent and solute, but especially, on the interactions between the molecules of the solute, the interactions between the molecules of the solvent and between the molecules of the binary solute-solvent pair. From among the presented values, the properties of the solvent and solute have the most important influence on the values of the molecular interaction parameters (*mip*). In order to be able to interpret the experimental results presented in this paper, we will refer to the Hansen solubility parameter values. The Hildebrand and Hansen solubility parameters play a very important part in the selection of the solvents used for various industrial applications. The Hildebrand solubility parameter is defined as the square root of the cohesive energy density, the heat of vaporization divided by the molar volume [8]. Hansen proposed an extension of the Hildebrand parameters so that they include three components: dispersion bonding energy, of the polar bonds and of the hydrogen bonds between the molecules [9]. The Hansen solubility parameters for the solvents used in these work are presented in Table 6.

Table 6. The Hansen solubility parameters for *DMF, NMP* and *PG* [10].

Solvent	δ_D, dispersive bonding parameter, MPa$^{0.5}$	δ_P, polar bonding parameter, MPa$^{0.5}$	δ_H, hydrogen bonding parameter, MPa$^{0.5}$	δ_T, total solubility parameter, MPa$^{0.5}$
Dimethylformamide	8.5	6.7	5.5	12.1
N-methylpyrrolidone	8.8	6.0	3.5	11.2
Propylene glycol	16.8	9.4	23.3	30.2

The analysis regarding the interaction parameters of propylene and propane in different solvents, and the Hansen solubility parameters, lead to the following conclusions:

• for saturated gases, as in the case of propane, the interaction parameter depends only on the strength of the intermolecular bonds of the solvent and on the number of "gaps" and "spaces" in which the gas should flow. From among the studied solvents, *PG* has the strongest hydrogen bonds, followed by the *DMF* and by the *NMP*. The solubility of propane, and its interaction parameter with the respective solvents, decreases in order: *NMP>DMF>PG*;

• for propylene, a gas with an ability to react higher than propane caused by its double hydrogen bond, solubility depends on the interaction between the solute and the solvent. In the case of the *DMF*, the dispersive forces between its molecules are weaker than in the case of the *NMP*, but the polarity of the molecules is higher, which makes the propylene polar molecules join and this results in an induced attraction (the induced dipole-dipole bond) between the *DMF* and the propylene and this leads to the increase of propylene solubility in *DMF*. From this point of view, *PG*, having the strongest dipole bonds between its molecules, should induce also the strongest dipole-dipole bond with the propylene molecules. But, the strong hydrogen bonds and the small "spaces" between the *PG* molecules, finally lead to the decrease of propylene solubility. In conclusion, the solubility of propylene, as its interaction parameter with the respective solvents, decreases in order: *DMF>NMP>PG*;

• at the same temperature, for the same solvent (for example: *DMF*, at the temperature of 293.15K), the *mip* for propylene is 0.3341, and in the case of propane it is 0.1356. The high difference between the interaction parameters of propylene and propane display the different reaction of gases (with the same carbon atoms number), the higher level of directness of the solvent in the detriment of the unsaturated hydrocarbon, thing that is reflected on the selectivity of the separation process of the two hydrocarbons through the operation of absorption; at the same temperature (for example at 293.15 K), the propylene interaction parameter with *DMF* is 0.3341, with *NMP* it is 0.2543, and in the case of the *PG* it is situated at the value of 0.1195. This comparison reflects the fact that from among the most common solvents, the most appropriate for the industrial process of separating propylene from the mixture with propane, is *DMF*.

Conclusions

The solubility of gases in solvents is a complex phenomenon to which a multitude of factors concur. The selection of the solvent which is the most appropriate in order to separate propylene from propane from within different gas fluxes through the process of absorption, is very difficult because we must keep in mind the pressure and temperature conditions that favors this process and, of course, the interaction between the solute and solvent.

In the present paper, propylene and propane solubility data have been shown, in the conditions on mixtures with three solvents: dimethylformamide, *N*-methylpirrolidone and propylene glycol, at three temperatures: 293.15, 313.15 and 333.15 K and a relative constant pressure (306…368 kPa). In order to appreciate the absorption behavior of the two gases in the enumerated solvents, a value proposed by Hayduk and Wong [5], was used, a term named "molecular interaction parameter". This term can be calculated with the help of a simple equation, as the ratio between the solubility of the solute in the liquid absorbent (expressed as molar fraction), in an environment of ideal and no ideal behavior of the liquid phase. In other words, this value shows the deviation from the ideal of the solute in the presence of the solvent, and the inversion of the solute's activity coefficient. Using this such simple value, that incorporates the effect of the intermolecular interactions from within each gaseous component, a value of the interactions between each solute-solvent binary, has proved to be a very effective tool for the selection of the solvent in the presence of which the separation of propylene from propane is the most favorable, from the technological and economical point of view.

 As a result of the analysis of the experimental data presented in this paper, and as a result of propylene and propane interactions in the tested solvents, we have reached the conclusion that the most appropriate solvent for our purpose is dimethylformamide.

References

1. S t r ă t u l ă , C . , *Fracţionarea, Principii şi Metode de Calcul*, Ed. Tehnică, Bucureşti, 1986, p. 165;
2. P e t r e , M . , *Studiul recuperarii hidrocarburilor nesaturate din gazele de rafinarie*, Teza de doctorat, iunie 2006
3. P e t r e , M . , S t r ă t u l ă C . , *Study of vapor-liquid equilibrium for propylene-propane binary in presence of two solvents*, Romanian International Conference on Chemistry and Chemical Engineering XIV, vol. 2, Bucharest, 22-24 sept. 2005, p.147.
4. P e t r e , M . , S t r ă t u l ă C . , *Influenta continutului de apa in solventii n-metilpirolidona si dimetilformamida asupra solubilitatii propilenei si propanului*, Revista de chimie, Bucuresti, 2007
5. H a y d u k , W . , W o n g , C - F . , *Solubility of Propylene Gas in Octane and Various Polar Solvents*, The Canadian Journal of Chemical Engineering, vol. 68, august, 1990, p.653.
6. www.en.wikipedia.org
7. R e i d , R . C . , P r a u s n i t z , J . M . , P o l i n g , B . E . , *The Properties of Gases and Liquids*, 4th Ed., McGraw-Hill, New York, 1988.
8. H i l d e b r a n d , J . H . *The Solubility of Non-Electrolytes*; New York: Reinhold, 1936.
9. H a n s e n , C h . , *Hansen Solubility Parameters: A user's handbook*. Boca Raton, Fla: CRC Press. ISBN 0-8493-1525-5, 2000. Retrieved from

   http://en.wikipedia.org/wiki/Hansen_Solubility_Parameters"
10. B u r k e , J . , *Solubility Parameters: Theory and Application*, The Oakland Museum of California, August 1984, www.google.com

Influența interacțiunilor moleculare asupra solubilității propilenei și propanului în diferiți solvenți

Rezumat

Lucrarea de fata prezinta un studiu experimental privind solubilitatea propilenei și propanului in trei solventi cu multiple aplicatii industriale: n-metilpirolidona (NMP), dimetilformamida (DMF) si propilenglicol (PG), la temperaturile de 293.15, 313.15 si 333.15 K si presiuni de 306...368 kPa. Solubilitatea propilenei si propanului depinde nu numai de temperatura si presiune, dar si de natura chimica a solventului. Pentru a compara rezultatele experimentale si a pune in evidenta efectul naturii solventului, solubilitatea propilenei și propanului se exprima sub forma parametrului de interactiune moleculara (pim). La aceeasi temperatura si presiune, efectul naturii solventului poate fi sumarizat astfel:

pim *propilena in DMF>* pim *propilena in NMP>* pim *propilena in PG,*
pim *propan in NMP>* pim *propan in DMF>* pim *propan in PG.*