

SOLUBILITY OF PROPYLENE AND PROPANE GASES IN *N*-METHYLPYRROLIDONE AND DIMETHYLFORMAMIDE SOLVENTS

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Propylene and propane gases solubilities in *N*-methylpyrrolidone and Dimethylformamide anhydrous solvents have been measured at 20, 40, 60 °C and pressure range between 50.65 and 506.5 kPa. Reported mole fraction solubilities were used to determine the Ostwald coefficients for a gases partial pressure of 101.3 kPa.

INTRODUCTION

Separation technology of unsaturate hydrocarbons: ethylene, propylene and butenes from ethylene-ethane, propylene-propane, butene-butane fractions, obtained from refinery gases, are based on classical distillation at ordinary temperature or low temperature in case of ethylene and propylene or, in butene separation case from C₄ fraction, by extractive-distillation in presence of different selective solvents¹. Theoretically, propylene separation from propane could be performed also by extractive-distillation but, practically this thing is difficult and not interesting economically because, the extractive-distillation needs propane reflux at the top of the column which leads at obtaining of a high pressure with undesirable effects on the bottom column temperature, in a sense of a strong increasing of this, with effects in propylene-propane separation. That's why, for propylene-propane separation, when after separation process, propylene must be obtained in vapor phase for its using in different processes and, it was proposed a physical absorption process² at low pressure in presence of two absorbents used like solvents in a the extractive-distillation process: *N*-methylpyrrolidone (*NMP*) and dimethylformamide (*DMF*). As it is known, for modeling absorption process it is necessary to know the solubility date for propane-propylene system in presence of two absorbents, at different temperatures and pressures.

EXPERIMENTAL

Solubility measurements were performed using a proper construction equilibrium apparatus previously described³. The glass trap with 100 cm³ absorbent is introduced in equilibrium cell at constant a experimental temperature ensured with a water bath. The cell is depressuring at absolute pressure below 1 mmHg by using the vacuum pump. The depressuring line is closed and the gas charged is slowly open from gas reservoir. The inlet pressure of the gas is read at digital manometer DPI 705 (Druck Limited England) with an accuracy of ±0,1 kPa. The charged gas is made in a way in which, at the impact of the gas with glass trap with absorbent, this remains intact. This operation (depressuring- filling with gas) is repeated two times for being sure that in the equilibrium cell is only gas, and not air. After the second operation, one can wait for half an hour so the glass trap- gas system approaches the desired temperature for experimental determination. The temperature (*T*) was controlled by Rotronic Thermotrol within ±0,01°C. In this moment it is read the pressure from the cell which is considered the initial pressure (*P_i*) of the gas before starting the absorption in the liquid. Then, the equilibrium cell is suddenly mixed so that the glass trap with absorbent can be broken and in this way the gas solubilization in the absorbent is done. Then we may stir for 1 hour until the pressure remains constant so that the equilibrium state can be reached. At the end of the determination the equilibrium pressure (the final pressure - *P_f*) is recorded with the same DPI 705, and after than the equilibrium cell is released from gas reservoir. All the experiments were performed at least three time to ensure good accuracy, replicate measurements gave results consistently within 1% of the mean value.

The propylene and propane gases were purchased from Linde Gas Bucharest at purity of 99.8 % weight. The *DMF* solvent was obtained from Merck-Schuchardt with 99.0 % weight purity and the *NMP* solvent was obtained from Carom-Onesti with 98.0 % weight purity.

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During the performing of the experiments, special precautions were taken with the solvents, particularly with the *DMF* solvent. This solvent is considered dangerous if inhaled or contacted. The solvents were exposed to the air for a minimum duration of time only, and any fumes or vapors released were vented to the fume hood. The complete solubility apparatus was mounted in a fume hood.

From experimental data, is calculated the solubility of these two gases in absorbent (in molar fraction), based on the gases law, for the initial moment (for the gas from the cell before the glass is broken) and also, for the final moment (after the glass trap is broken and reaches the equilibrium). No *NMP* or *DMF* were considered in vapor phase because at the experimental temperatures vapor pressures of both solvents are insignificant. So:

$$P_i V = z_i n_i RT \quad (1)$$

$$P_f V = z_f n_f RT \quad (2)$$

Considering that the gas volume is constant (cell volume), by decreasing the equation (2) from the equation (1), is obtained:

$$\Delta PV = \Delta n RT \quad (3)$$

From equation (3) it is calculated the number of moles solubilised gas, noted only with "n", in assumption that the compressibility factors z_i and z_f are practically equals:

$$n = \frac{\Delta PV}{RT} \quad (4)$$

In this case, molar fraction of solubilized gas is calculated with equation:

$$x = \frac{n}{n + n_{\text{absorbant}}} \quad (5)$$

RESULTS AND DISCUSSION

Data for the solubility of propylene and propane in *NMP* and *DMF* anhydrous were obtained at following temperatures: 20, 40, 60°C and pressures between 50.65 and 506.5 kPa. The results are presented in figures 1 and 2. The data were correlated using Soave-Redlich-Kwong (*SRK*) equation. The optimum interaction parameter, k_{ij} , in the mixing rule of the equation of state was obtained by minimizing the error in the predicted bubble point pressure.

$$f(k_{ij}) = \sum \left| \frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right| \cdot \frac{100}{N} \quad (6)$$

where P_{exp} is the experimental bubble point pressure, P_{calc} is the calculated bubble point pressure and N is the number of data points. The solubility data were well-correlated by Soave-Redlich-Kwong equation of state. The maximum mean absolute deviation was 1.31%.

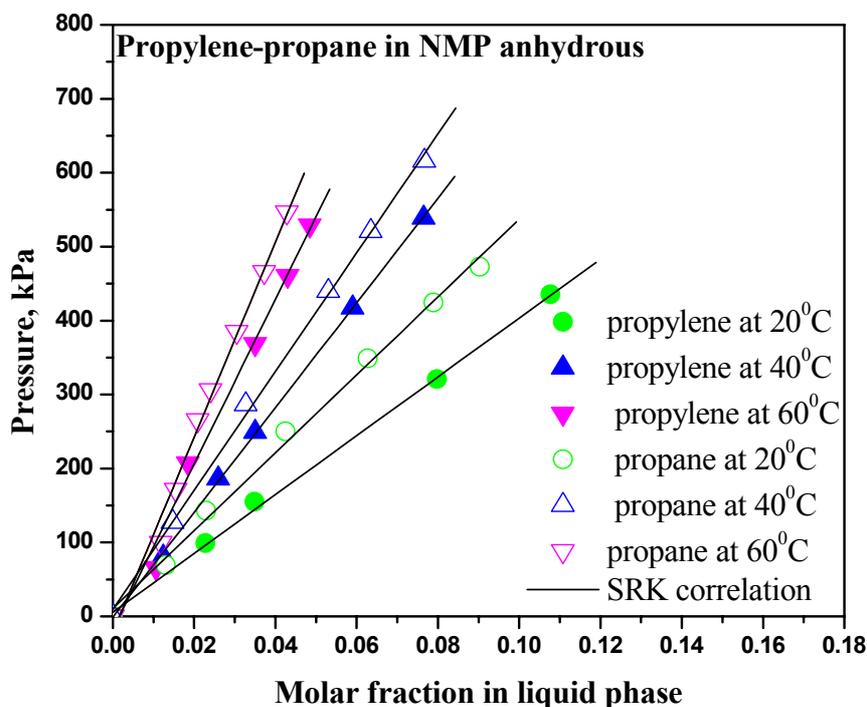


Fig. 1 – The solubility propylene and propane in *NMP* anhydrous.

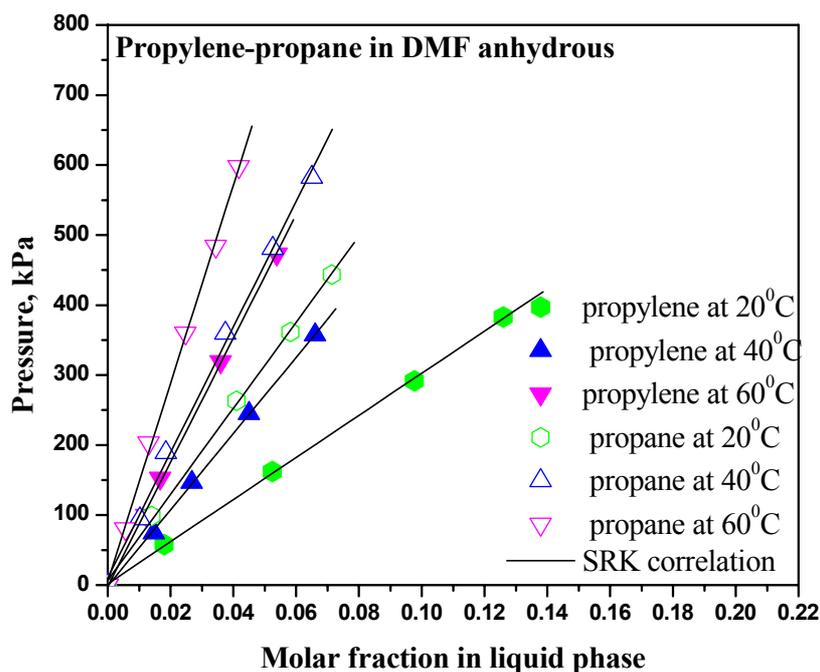


Fig. 2 – The solubility propylene and propane in *DMF* anhydrous.

The mole fraction solubilities were used in order to calculate the Ostwald coefficients for the propylene and propane gases in both solvents for a gas partial pressure of 101.3 kPa. The Ostwald coefficient, defined by the volume of pure gas and volume of solvent which, when we mix them together at experimental temperature and pressure, will produce a saturated solution. This coefficient is clearly defined and can be readily calculated from experimental data.

The Ostwald coefficient (L) as defined for a gas partial pressure (p) of 101.3 kPa can be determined from the mole fraction solubility (x_1):

$$L = \frac{101.3 V_G x_1}{[P V_L (1 - x_1)]} \quad (7)$$

where P is total experimental pressure, V_G is molar volume of gas, V_L is molar volume of saturated solvent.

Because the *NMP* and *DMF* solvents are non-volatile at experimental temperatures ($p = P$), this means that Ostwald coefficient is independent of pressure.

The molar volumes of propylene and propane gas at experimental temperatures were calculated using Soave-Redlich-Kwong equation of state and *PRO-II* Simulator. The results are presented in Table 1.

The saturated molar volumes of solvents were calculated with an equation developed by Rackett and modified by Spencer and Danner⁴.

$$V_L = \frac{R T_C}{P_C} Z_{RA}^{[1+(1-T_R)^{2/7}]} \quad (8)$$

where T_C (in K) and P_C (in bar) are critical properties of pure solvents, T_R is reduced temperature in K and Z_{RA} is a constant. If Z_{RA} values are not listed in literature, they may be estimated by equation⁵:

$$Z_{RA} = 0.29056 - 0.08775\omega \quad (9)$$

where ω is acentric factor of solvent.

The critical properties and the acentric factors for *NMP* and *DMF* were listed from *PRO-II* Simulator Database⁶ and used in equations (9) and (8) for molar saturated volumes calculus. The results are presented in Table 2.

Propylene and propane solubilities in *NMP* and *DMF* solvents are reported both as the mole fraction solute and as the Ostwald coefficients for a gas partial pressure of 101.3 kPa. For temperatures from 20 °C to 60 °C these data are graphically represented in Figure 3. A comparison, with Hayduk data from the literature⁷ is made only for propylene solubilities in *DMF*.

Table 1

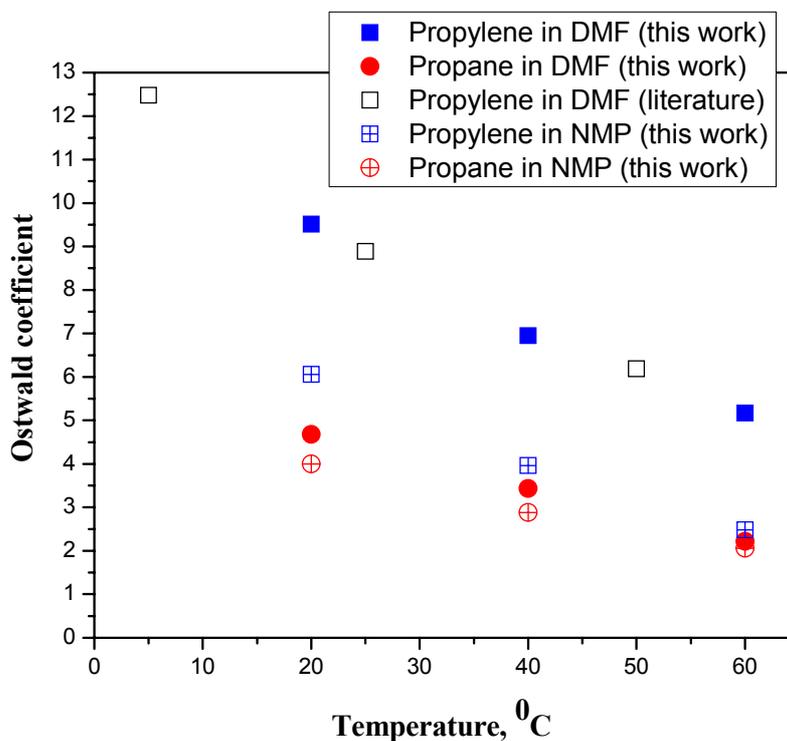
The molar volumes of propylene and propane gas

Temperature, °C	Propylene $V_G, \text{m}^3/\text{kmol}$	Propane $V_G, \text{m}^3/\text{kmol}$
20	23.71	23.66
40	25.39	25.35
60	27.07	27.04

Table 2

The molar saturated volumes of *NMP* and *DMF*

Temperature, °C	<i>NMP</i> $V_L, \text{m}^3/\text{kmol}$	<i>DMF</i> $V_L, \text{m}^3/\text{kmol}$
20	0.09617	0.07707
40	0.09768	0.0784
60	0.09923	0.0798

Fig. 3 – Propylene and propane Ostwald coefficients in *NMP* and *DMF*.

From figure 3 result that Ostwald coefficients of propylene and propane decreases with temperature increase. The Ostwald coefficients of propylene is higher than of propane. On the other hand, at the same temperature, the Ostwald coefficients of propylene and propane in *DMF* is higher than in *NMP*.

Ostwald coefficients of propylene in *DMF* from this work are in good agreement with the reported

data in literature because, together, describe a good variation curve with temperature.

CONCLUSIONS

In this work were reported experimental solubility data for propane and propylene in the *NMP* and *DMF* anhydrous absorbents at different

temperatures and pressures. From the solubility data, Ostwald coefficients were calculated at 101.3 kPa. The graphically represented results indicated that the *DMF* absorbent is better than *NMP*.

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