

THE POTENTIAL OF SOAVE-REDLICH-KWONG EQUATION OF STATE IN DESCRIBING PHASE EQUILIBRIA DATA AT HIGH PRESSURES FOR THE CO₂ + 1-ALCOHOL SYSTEMS

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The Soave-Redlich-Kwong equation of state with simple quadratic mixing rule using only one mixture parameter, k_{ij} , was tested as for the representation of vapour-liquid-liquid equilibria in binary carbon dioxide–1-alcohol systems. The necessary parameters for the description of the selected experimental data of carbon dioxide–1-alcohol systems are reported and the results of the correlation and prediction are discussed.

INTRODUCTION

During the last years, significant interest has been paid to separation processes where a condensed phase (liquid or solid) is in contact with a fluid phase that is supercritical (in respect to one of the components) both in temperature and in pressure. Various fluids have been investigated for use as solvents in supercritical fluid chromatography (SFC) and supercritical fluid extraction (SFE). However, the most popular and safe supercritical fluid is undoubtedly carbon dioxide. It is non-flammable, chemically inert, odour free, available with high purity at low cost, and there is no disposal problem. Alcohols are used in order to control the polarity of supercritical fluid solvents in SFE and as modifiers for SFE. By adding a co-solvent like alcohols to petroleum fluids the formation of undesired hydrates can be prevented. Moreover, alcohol recovery can be carried out using SFE. For all these reasons, it is necessary to know the phase behaviour of the carbon dioxide–alcohol systems.

At low and moderate pressures, extensive systematic experimental studies have been done previously for other various organic mixtures^{1–6} where excess Gibbs energy models have been successfully used for their description. At high pressures, equations of state were used.⁷

Soave-Redlich-Kwong equation of state (SRK EOS) is one of the most popular models for the correlation of phase equilibria at high pressures. Even for complex systems, the literature shows that this equation works quite well. The equation was successfully tested recently for description of the carbon dioxide and nitrogen solubility in alternative fuels such as methanol and dimethyl ether⁸ or for mixtures of alternative refrigerants as fluorohydrocarbons with lubricant oils.⁹ When critical parameters of the pure compounds and interaction parameters for the binary mixtures are known, the SRK EOS may be used in the process simulators by industry for the prediction of thermodynamic properties of multicomponent systems of different complexity. Simplicity of the equation ensures the time saving in the computations.

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In this work, SRK EOS with quadratic mixing rule is tested for the first time for the description of gas solubility or vapour-liquid equilibria (VLE) data for systems of CO₂ + 1-alcohols at high pressures. The required parameters for the process simulators are presented in this paper. The calculations were performed using professional worldwide used software, PE2000,¹⁰ for correlation and prediction of phase equilibria.

THERMODYNAMIC MODEL

Despite of the general imperfection of cubic equations of state in providing the PVT data, the phase equilibrium in mixtures is usually well described. It is well known that the simple EOS of cubic type can correlate P - T - x - y (pressure-temperature-compositions) data in VLE or VLLE (vapor-liquid-liquid equilibria) with sufficient accuracy. Generally, an equation of state has a sound theoretical basis and can be derived based on the virial expansion up to the second order, together with physically reasonable assumptions.¹¹

In the present work, we selected the SRK equation of state¹² for testing and modeling of the carbon dioxide solubility in 1-alcohols at high pressures. This choice was made due to its good performance in a wide range of applications.

The equation is written in the following form

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (1)$$

where the parameters for pure compound i can be evaluated from critical temperature and pressure, T_c , P_c , and acentric factor, ω , as follows

$$a(T) = a_i(T) = a_c \alpha(T) \quad (2)$$

where

$$a_c = 0.42747 \frac{R^2 T_c^2}{P_c} \quad (3)$$

$$\alpha(T) = \left(1 + m \left(1 - \sqrt{T_r}\right)\right)^2 \quad (4)$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2 \quad (5)$$

and

$$b = b_i = 0.08664 \frac{RT_c}{P_c} \quad (6)$$

For mixtures, the quadratic mixing rule offers maximum two binary interaction parameters per binary system, but usually only one is used to adjust the parameter a . All the other mixing rules available in PE2000¹⁰ for EOS's offer maximum three adjustable binary parameters, from which two are used to adjust the parameter a . These mixing rules are reduced exactly to the quadratic mixing rule if the third parameter is not used, *i.e.* set to zero. Often, the quadratic mixing rule is sufficient for correlation of equilibria in systems that do not contain specific interactions. In this work, the use of the second adjustable parameter l_{ij} is eliminated by setting all $l = 0$. Therefore, the parameters for the studied mixtures are evaluated using quadratic mixing rules involving pure component data and binary interaction parameters k_{ij} :

$$a = \sum_i \sum_j x_i x_j (1 - k_{ij}) \sqrt{a_i a_j} \quad \text{with} \quad k_{ij} = k_{ji} \quad (7)$$

$$b = \sum_i \sum_j x_i x_j \frac{b_i + b_j}{2} (1 - l_{ij}) \quad \text{with} \quad l_{ij} = l_{ji} = 0. \quad (8)$$

The binary interaction parameters k_{ij} have been adjusted in the routine of the flash calculation in which the compositions of liquid and vapour phases at constant temperature have been evaluated from P - T data using the sum of the absolute deviations in the liquid phase as an objective function, namely.

$$obj.funct. = \frac{1}{n} \sum_{i=1}^n |x_{li}^{exp} - x_{li}^{calc}| \quad (9)$$

where n is number of the experimental points and superscripts *exp*, *calc* denote experimental and calculated values, respectively. The optimization method used for the binary parameters determination is the simplex Nelder-Mead algorithm.¹³

EXPERIMENTAL DATABASE

The mixtures under study include carbon dioxide + methanol¹⁴, + ethanol¹⁵, + 1-propanol¹⁶, + 1-butanol¹⁷, + 1-pentanol¹⁸, + 1-octanol¹⁹, + 1-nonanol²⁰, + 1-decanol²¹, + 1-dodecanol²², + 1-tetradecanol²³, + 1-hexadecanol²³ and + 1-octadecanol²³. The extension of the database has been made by considering the liquid-liquid equilibria data²⁴ for carbon dioxide + 1-hexanol, + 1-octanol and + 1-decanol. The selection of the experimental data has been made based on the criteria of the confidence in the authors, the quality of the journal that published the data and the completeness of the data sets (pressure P , temperature T , mole fraction of the single liquid phase and of the vapour or second liquid phase, respectively).

RESULTS AND DISCUSSION

The critical temperature, T_c , critical pressure, P_c , and acentric factors, ω , literature data²⁵ of pure compounds are presented in Table 1.

Table 1

Critical temperature, T_c , critical pressure, P_c , and acentric factors, ω , for pure compounds

Compound	Formula	T_c (K)	P_c (MPa)	ω
Carbon dioxide	CO ₂	304.1	7.38	0.239
Methanol	CH ₃ OH	512.6	8.09	0.556
Ethanol	CH ₃ CH ₂ OH	513.9	6.14	0.644
1-Propanol	CH ₃ (CH ₂) ₂ OH	536.8	5.17	0.623
1-Butanol	CH ₃ (CH ₂) ₃ OH	563.1	4.42	0.593
1-Pentanol	CH ₃ (CH ₂) ₄ OH	588.2	3.91	0.579
1-Octanol	CH ₃ (CH ₂) ₇ OH	652.5	2.86	0.587
1-Nonanol	CH ₃ (CH ₂) ₈ OH	671.0	2.61	0.635
1-Decanol	CH ₃ (CH ₂) ₉ OH	687.0	2.22	0.621
1-Dodecanol	CH ₃ (CH ₂) ₁₁ OH	679.0	1.92	1.019
1-Tetradecanol	CH ₃ (CH ₂) ₁₃ OH	702.7	1.76	1.131
1-Hexadecanol	CH ₃ (CH ₂) ₁₅ OH	724.4	1.57	1.181
1-Octadecanol	CH ₃ (CH ₂) ₁₇ OH	747.1	1.41	1.234

The results of the correlation of experimental data with the use of SRK EOS are summarized in Table 2. Here, only the vapour-liquid equilibria data were considered, except for the system carbon dioxide–1-nonanol for which liquid-liquid equilibria data were used.

The correlation was carried out in two steps regarding the temperature of the system: the *individual correlation*, *i.e.* independent evaluation of each isotherm, and the *global correlation*, where the calculation assumes that the interaction parameter k_{ij} is temperature independent and calculated as a weighted mean

average of those obtained in the individual correlation. For the systems studied, the differences between the individual or the global correlation results are not significant. Therefore, only the results of the global correlation are shown in Table 2. The deviations between the experimental and the calculated data are given as absolute average deviations in mole fraction of the liquid phase $AADx_1(x_1^{L1}, x_1^{L2})$ or of the vapour phase $AADy_1$.

Table 2

Results of the experimental data correlation for CO ₂ + 1-alcohol systems with SRK EOS				
System of CO ₂ with	T, K	k_{ij}	$AADx_1(x_1^{L1})$	$AADy_1(x_1^{L2})$
CH ₃ OH	230–330	0.0634	0.101	0.051
CH ₃ CH ₂ OH	312.82–391.96	0.0881	0.045	0.042
CH ₃ (CH ₂) ₂ OH	322.36–352.83	0.0877	0.043	0.020
CH ₃ (CH ₂) ₃ OH	314.16–422.03	0.0997	0.029	0.010
CH ₃ (CH ₂) ₄ OH	329.45–412.26	0.0894	0.047	0.044
CH ₃ (CH ₂) ₇ OH	313.15–348.15	0.1068	0.083	0.089
CH ₃ (CH ₂) ₈ OH	303.15	0.1114	(0.010)	(0.015)
CH ₃ (CH ₂) ₉ OH	348.15–453.15	0.1554	0.031	0.034
CH ₃ (CH ₂) ₁₁ OH	392.15	0.0609	0.024	0.010
CH ₃ (CH ₂) ₁₃ OH	373.15–473.15	0.0252	0.073	0.078
CH ₃ (CH ₂) ₁₅ OH	373.15–573.15	0.0600	0.017	0.010
CH ₃ (CH ₂) ₁₇ OH	373.15–573.15	0.0366	0.042	0.039

These deviations are small, but a little bit higher for the liquid phase in the case of carbon dioxide–methanol system. However, they are acceptable even for this system as is obvious from Fig. 1.

In Fig. 2, the comparison between the experimental VLE data and those calculated using the parameters from Tables 1 and 2 for the carbon dioxide–1-octanol system, is presented.

The same k_{ij} was used for prediction of the LLE of this system and the results are compared in Fig. 3 with the data experimentally determined by Lam *et al.*²⁴ The differences decrease with the increasing temperature, finally attaining an excellent representation at 306.15 K.

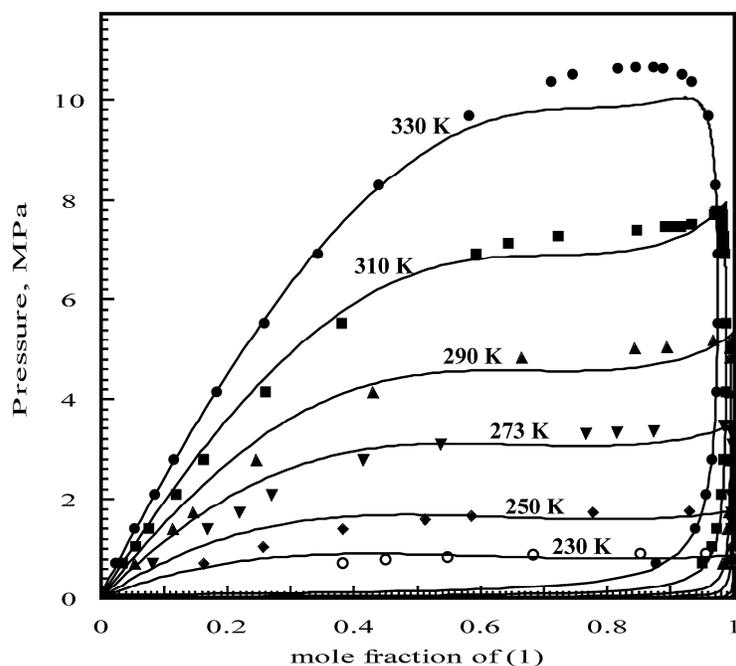


Fig. 1 – Comparison between predicted and experimental (P, x, y) data for carbon dioxide (1) + methanol (2) system at different temperatures. Symbols represent the experimental points¹⁴ at shown temperatures and full lines represent the calculated values with SRK EOS using $k_{ij} = 0.0634$ obtained from correlation.

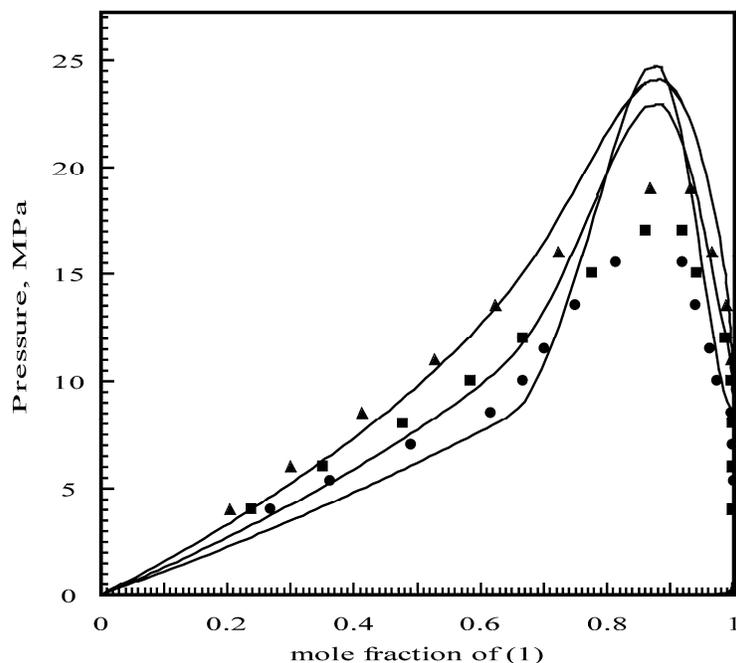


Fig. 2. - Comparison between predicted and experimental (P, x, y) data for carbon dioxide (1) + 1-octanol (2) system at different temperatures. Symbols represent the experimental points¹⁹ at 313.15 K (●), 328.15 K (■), 348.15 K (▲) and full lines represent the calculated values with SRK EOS using $k_{ij} = 0.1068$ obtained from correlation.

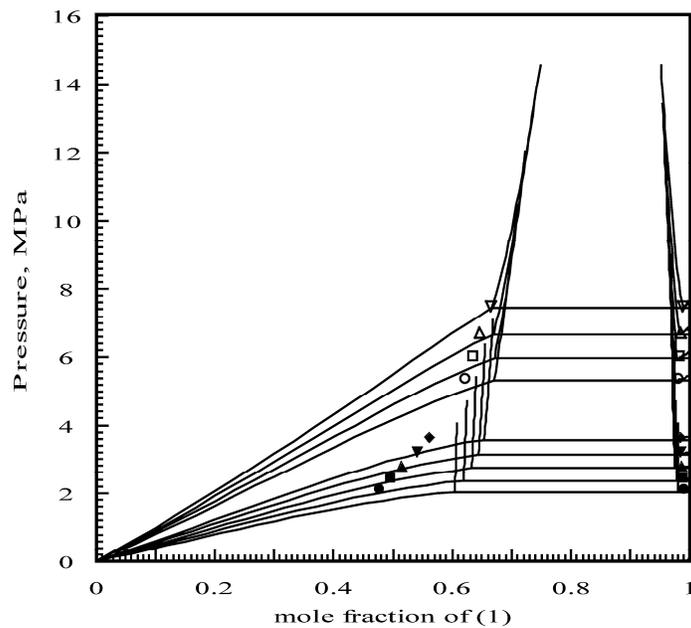


Fig. 3 - Comparison between predicted and experimental (P, x^{L1}, y^{L2}) data for carbon dioxide (1) + 1-octanol (2) system at different temperatures. Symbols represent the experimental points²⁴ at 255.15 K (●), 260.15 K (■), 265.15 K (▲), 270.15 K (▼), 275.15 K (◆), 291.15 K (○), 296.15 K (□), 301.15 K (Δ), 306.15 K and full lines represent the calculated values with SRK EOS using $k_{ij} = 0.1068$ obtained from correlation of VLE (P, x, y) data¹⁹.

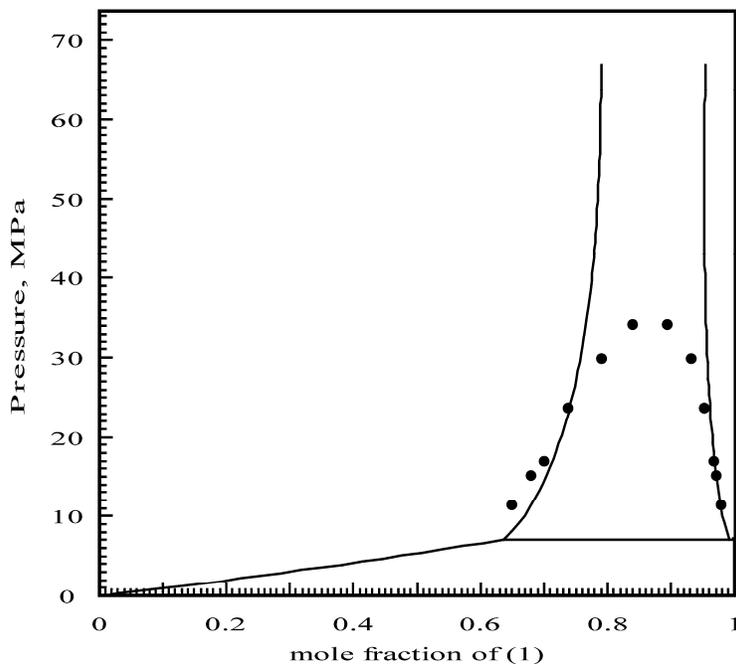


Fig. 4 - Comparison between predicted and experimental (P, x^{L1}, y^{L2}) data for carbon dioxide (1) + 1-nonanol (2) system at 303.15 K. Symbols represent the experimental points²⁰ and full lines represent the calculated values with SRK EOS using $k_{ij} = 0.1114$ obtained from LLE (P, x^{L1}, y^{L2}) correlation.

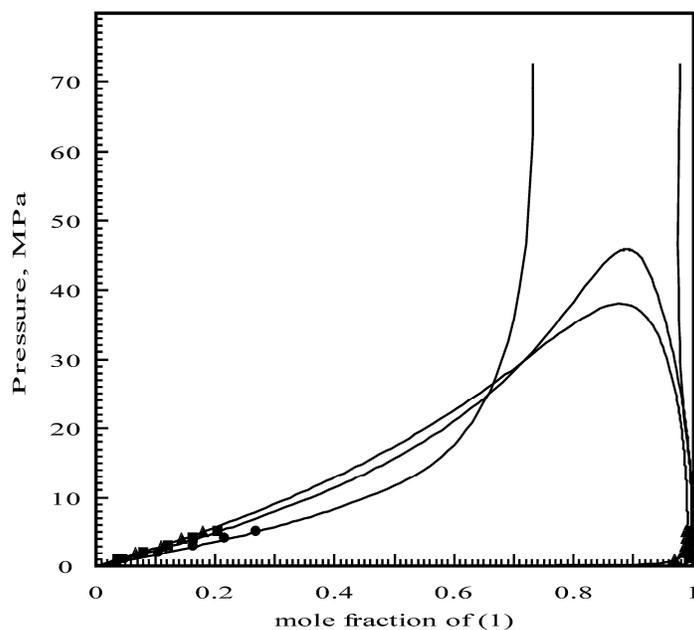


Fig. 5 - Comparison between predicted and experimental (P, x, y) data for carbon dioxide (1) + 1-decanol (2) system at different temperatures. Symbols represent the experimental points²¹ at 348.15 K (●), 403.15 K (■), 453.15 K (▲) and full lines represent the calculated values with SRK EOS using $k_{ij} = 0.1554$ obtained from correlation.

In Fig. 4, the results are given of the calculation using the evaluated parameters for the carbon dioxide–1-nonanol system, in comparison with the experimental LLE data at 303.15 K²⁰.

In Figs. 5 and 6, the similar comparisons as for the carbon dioxide–1-octanol system are presented for the carbon dioxide–1-decanol system. In this case, the LLE is better predicted at lower temperatures when the comparison is made with the experimental data of Lam *et al.*²⁴

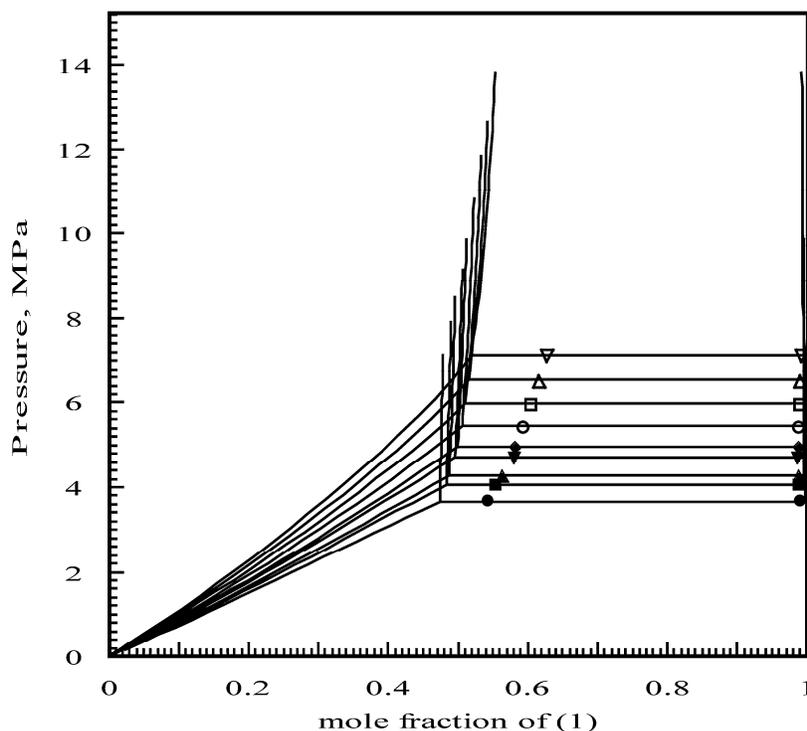


Fig. 6 – Comparison between predicted and experimental (P , x^{L1} , x^{L2}) data for carbon dioxide (1) + 1-decanol (2) system at different temperatures. Symbols represent the experimental points²⁴ at 275.15 K (∇), 279.15 K ($\#$), 281.15 K (\odot), 285.15 K (\otimes), 287.15 K (\oplus), 291.15 K (''), 295.15 K (v), 299.15 K (v), 303.15 K (v) and full lines represent the predicted values with SRK EOS using $k_{ij} = 0.1554$ obtained from correlation of VLE (P , x , y) data²¹.

Figs. 1–6 are examples of typical cases of the results of the phase behaviour prediction in CO₂ + 1-alcohol systems with SRK EOS and reflect the numerical values given in Table 2 for the experimental data correlation.

The quality of the VLE prediction for the carbon dioxide-1-alkanols at high pressures is generally good and the Soave-Redlich-Kwong equation of state proved to be a useful tool for description of phase equilibria.

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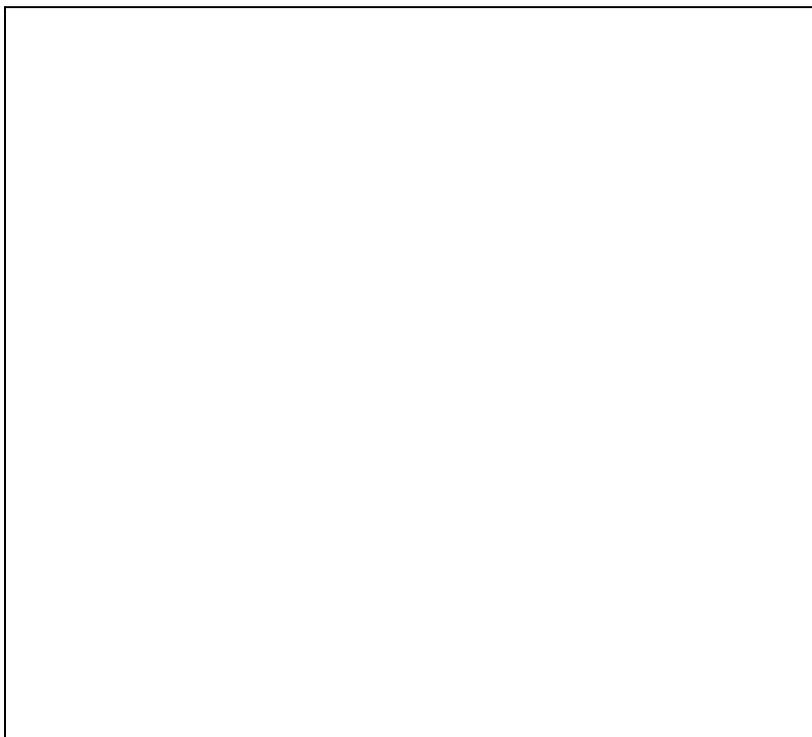


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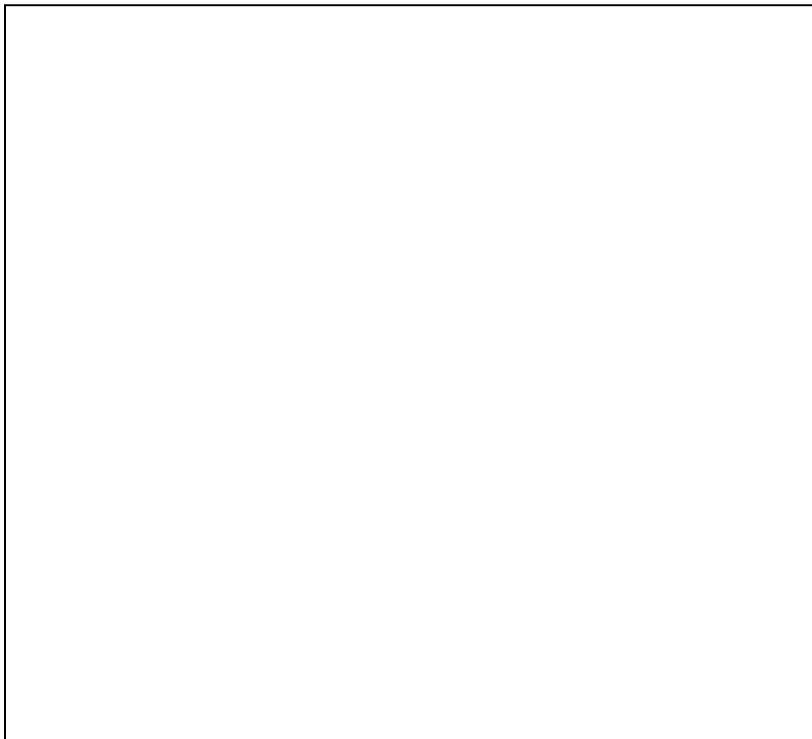


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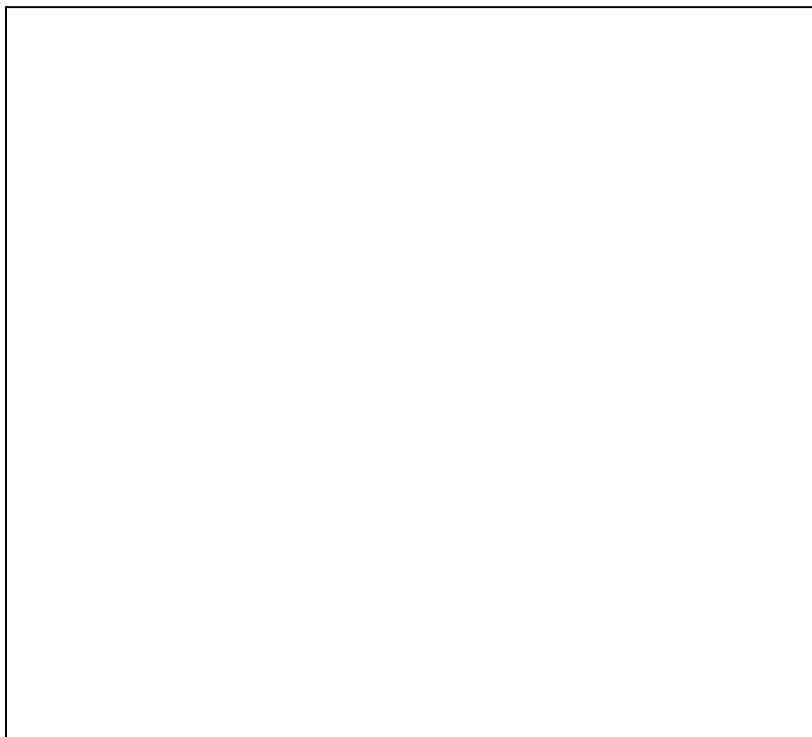


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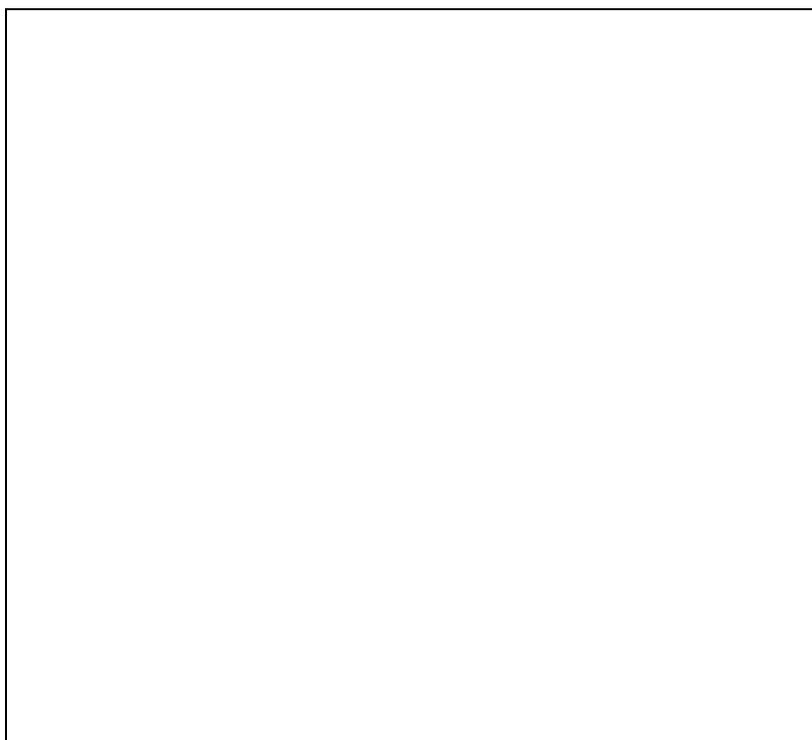


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