

MODELING OF ASKAREL SOLUBILITY IN SUPERCRITICAL CO₂ AIMING SOLID RESIDUE TREATMENT

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Abstract. Polychlorinated Biphenyls (PCBs) are chlorinated organic substances which are highly toxic and are also considered persistent organic pollutants (POPs). It should be emphasized the environmental importance for treating wastes with PCBs. For instance, Stockholm Convention on POPs established the elimination of the use of PCBs in equipments, e.g. electrical transformers and capacitors, by 2025. The decontamination of materials containing PCBs may be performed by supercritical extraction technology using carbon dioxide (CO₂) as solvent. The first objective of this work was the formulation of a computational tool to correlate solubility data of aromatic compounds in supercritical CO₂, using Peng-Robinson equation of state with fitted parameters. In a second step, a description of askarel oil, like araclor 1254, solubility in supercritical CO₂ was provided for simulation purposes of the extraction process. PCB mixture has predominance of congeners: penta, hexa, heptachloro biphenyl, tri and tetrachlorobenzene. The calculation procedure was initially used for a series of aromatic compounds (naphthalene, biphenyl, anthracene and phenanthrene) in order to test the approach. Experimental solubility data collection has been elaborated from the literature, providing a systematic series of binary and ternary data of the aromatic compounds with CO₂. The binary parameters for the mixing rule were systematically estimated, together with a new set of Clausius-Clapeyron solute vapor pressure to better describe the temperature dependence and achieve experimental uncertainties. Finally, the estimated parameters were used to simulate solubility values of the Askarel oil as function of the operational conditions of extraction by a simultaneous solution of the equilibrium equations for each compound. The thermodynamic modeling demonstrated to be feasible for process analysis and design.

Keywords: PCBs, Askarel, solubility, equation of state, supercritical fluid extraction

1. Introduction

Polychlorinated Biphenyls (PCBs) are chlorinated organic substances which are highly toxic and are also considered persistent organic pollutants. The high thermal and chemical stability of PCBs are responsible for their hard degradation, and when these substances are liberated in the environment, their accumulation in ecosystems leads to their incorporation in the food chain, exhibiting biomagnification [1].

PCBs structure and the amounts of chlorine atoms are important into determining levels of toxicity, in that the more harmful PCBs are those with highest number of chlorine atoms in the molecule. Although the

production of these substances had been banned, its presence in the environment is still found. In the 70s, PCBs were produced for specific purpose such as: thermal fluid in heat exchangers, lubricant in some equipment, isolating fluid in electrical equipment, resins, pesticides and others. Due to the high risk of this group of chemical substances the manufacture and the commercialization of PCB was forbidden [2,3].

The most used process for the treatment of a material containing organic contamination, like PCB, consists on the incineration in plasma ovens with double stage. However, beside the high energy demand, it should be considered the transport of the contaminated material until the place of the incineration; special conditions are required, increasing the global cost of the process [4-6]. In this context, the extraction process represents an important way to decrease significantly the mass and also the volume of the material to be transferred for treatment [7]. The supercritical fluid extraction (SFE) is considered to be a green technology due to shorter extraction times and less solvent exposure and disposal [8]. SFE seems to be adequate to the removal of the askarel oil impregnated in solid materials. An experimental series of SFE for PCB species with carbon dioxide as solvent and ethanol as co-solvent has been determined in the laboratory.

In this work, a thermodynamic modeling is presented to describe the solubility of the askarel in supercritical carbon dioxide as function of the operational conditions of extraction, i.e., temperature, pressure and composition, based on a series of experimental data selected and collected from the literature, not only for PCB species but also aromatic compounds [9-26].

2. Methods of calculation

In this work, a thermodynamic modeling is presented to describe the solubility of askarel oil in supercritical CO₂ as function of the operational conditions of extraction, i.e., temperature, pressure and composition. The askarel solubility is actually represented by the sum of the main species characterized or considered, calculating the concentration of the individual species in the multicomponent mixture [30].

The Scilab open source tool has been applied to perform the calculations with the aid of numerical methods included in the package, such as Levenberg-Marquadt Algorithm for the classical mixing rule parameter estimation [31].

Askarel oil is a mixture of polychlorinated biphenyls (PCBs) and chlorobenzenes containing various levels of chlorination. The analysis of a collected sample of askarel oil demonstrated predominance of the congeners tetra, penta, hexa and heptachlorobiphenyl [32]. Further, the askarel oil presented 25% in mass of tetrachlorobenzene, in which was described by 1,2-dichlorobenzene and hexachlorobenzene.

To determine normal boiling point, critical temperature and critical pressure of the main compounds found in the askarel, the Joback group contribution method has been applied [33]. The acentric factors (ω) were estimated by the Ambrose-Walton method [34].

A comprehensive series of experimental solubility data of aromatic, chlorinated aromatic and PCB congeners in SC-CO₂ has been collected from the literature in wide ranges of temperature and pressure. Therefore, the corresponding binary interaction parameters were estimated for the quadratic mixing rules for both attractive and repulsive parameters, with one adjusted parameter (k_{ij} and l_{ij}), respectively, using Peng-Robinson EoS [35,36].

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}; \quad a_{ii} = 0.45724 \frac{R^2 T_{c,i}^2}{P_{c,i}} \alpha; \quad \alpha = \left[1 + f(\omega) \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2; \quad b_{ii} = 0.0778 \frac{R T_{c,i}}{P_{c,i}} \quad (1)$$

$$a = \sum_{i=1}^c \sum_{j=1}^c y_i y_j a_{ij}; \quad a_{ij} = a_{ji} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij}); \quad b = \sum_{i=1}^c \sum_{j=1}^c y_i y_j b_{ij}; \quad b_{ij} = b_{ji} = \frac{b_{ii} + b_{jj}}{2} (1 - l_{ij}) \quad (2)$$

The solubility of a solute species in a supercritical fluid (ScF) may be calculated as described by Equation 3 at moderate and high pressures.

$$y_i^{ScF} = \frac{P_i^{sat}}{P} \left(\frac{1}{\phi_i^{ScF}} \right) \exp \left[\frac{v_i^{sat} (P - P_i^{sat})}{RT} \right] \quad (3)$$

Equation 3 is the solubility equation and it may be classified as three contributions, i.e., ideal solubility - defined as the ratio of the vapor pressure upon the total pressure -, fugacity coefficient that is evaluated by the

EoS and take into account the nonidealities, and finally Poynting factor which express the fugacity correction in respect to the pressure. The last two terms together is also called enhancement factor (E) that express the gain of solubility by operating in supercritical conditions, usually at high pressures. It is noteworthy that equation 3 may be solved for the solubility (y_i) by an iterative procedure since the solute mole fraction is also a variable in the fugacity coefficient.

$$y_i^{ideal} = \frac{P_i^{sat}}{P}; \quad E = \frac{1}{\phi_i^{ScF}} \exp\left[\frac{v_i^{sat}(P - P_i^{sat})}{RT}\right] \quad (4)$$

$$y_i^{ScF} = \frac{P_i^{sat}(T)}{P} E(T, P, y_i) = y_i^{ideal}(T, P) E(T, P, y_i) \quad (5)$$

It is also worthwhile that it was required the evaluation of the vapor pressure and molar volume of the solute as function of the temperature, which is present in the solubility equation in the ideal solubility term and enhancement factor, respectively. For that Clausius-Clapeyron correlation of the available experimental or estimated vapor pressure data was made for each compound. Vapor pressure data for the studied species were found in the literature [37-39].

$$P_i^{sat} = \exp\left(A - \frac{B}{T}\right) \quad (6)$$

Racket equation of state was used to describe the molar volume of these species [40]. A correction from the liquid phase for the solid phase was applied especially for, considering the experimental values of molar volume of a series of aromatic compounds. The series of aromatic compounds was naphthalene, biphenyl, phenanthrene and monochlorobenzene. The obtained correction factor obtained was 0.87 ± 0.04 to evaluate the molar volume of the solid phase from the values of the liquid phase. The experimental values of molar volume of both liquid and solid phases were retrieved from the AIChE DIPPR databank [39].

$$v_i^{sat} = 0.87 v_{c,i} (0.29056 - 0.08775\omega_i)^{(1-T_{r,i})^{2/7}} \quad (7)$$

Previous work has considered the mixture as a pseudo-binary system consisting of askarel and CO₂. In other words the askarel was “lumped” as tetrachlorobenzene, hexachlorobiphenyl and heptachlorobiphenyl. The askarel properties was obtained as mole fraction mixing rule [41]. In this work, the main components of the askarel have been considered and the solubility equation for each solute was simultaneously solved, finding the corresponding equilibrium concentrations (y_i). Then askarel solubility is finally the summation of these main solute species concentrations considered.

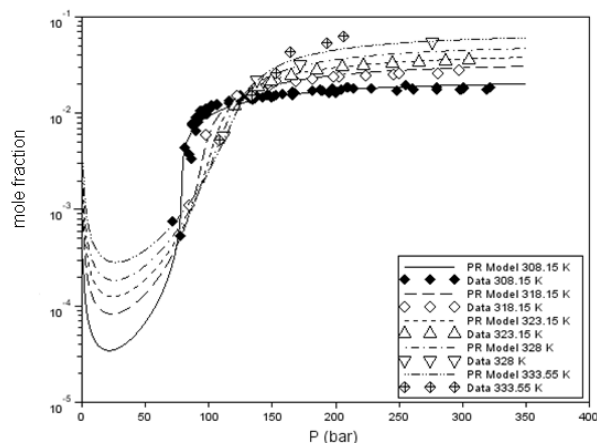
3. Results and discussions

The computational approach needed to be validated with experimental data published in the literature for conventional systems. This has been tested with four binary systems in the presence of supercritical CO₂: naphthalene [11-17], biphenyl [11,18-20], phenanthrene [21-23] and anthracene [22,24-25]. Naphthalene has been chosen as an example for this validation procedure. Figure 2 presents solubility correlation for this system, demonstrating feasibility with respect to the experimental uncertainty and also agreement with Sandler [36]. Furthermore, the objective function applied was the relative or the logarithmic with respect to experimental and calculated solubilities. This was due to the low magnitude of the values of solubility and its variation along the pressure of the datasets. The evaluation has been according to the absolute average relative deviation (AARD), Equation 8, and a comparison of the root mean square deviation of these correlations demonstrated to approach the experimental uncertainties.

$$\text{AARD}(\%) = \frac{100}{N} \sum_{i=1}^N \frac{|y_i^{\text{exp}} - y_i^{\text{calc}}|}{y_i^{\text{exp}}} \quad (8)$$

In order to describe the solubility behavior of the askarel oil in supercritical carbon dioxide, a selection of the predominant compounds was made. Table 1 presents the required thermodynamic properties of the askarel compounds used in the calculation. Joback contribution method was applied to determine the properties of the three representative species of askarel [33-34]. As it may be observed for other aromatic chlorinated compounds, the melting point increases as the number of radical chlorine increase. For the PCB compounds this is also true as it may be detected in Table 1.

Using the proposed methodology, the solubility data of the hexachlorobiphenyl and heptachlorobiphenyl were correlated with PR EoS, estimating the corresponding binary interaction parameters and Clausius-Clapeyron constants, as may be observed in Figures 2 and 3.



T (K)	308-333
k_{ij}	0.099
AARD (%)	16.94
k_{ij}	-0.011
l_{ij}	-0.154
AARD (%)	12.0
k_{ij}	-0.042
l_{ij}	-0.202
A	33.84
B	9389.45
AARD (%)	9.8
Data Points	150

Figure 1 - Solubility of naphthalene in supercritical CO₂ as function of the pressure, using the Peng-Robinson (PR) EoS with estimated k_{ij} equals to 0.099 (AARD = 17%). Sandler [36] value of k_{ij} equals to 0.103 (AARD = 26%). The correlation presented in the plot has 150 experimental values retrieved from the literature [11-17] and the lines represent the modeling with four fitted parameters (AARD = 9.8%).

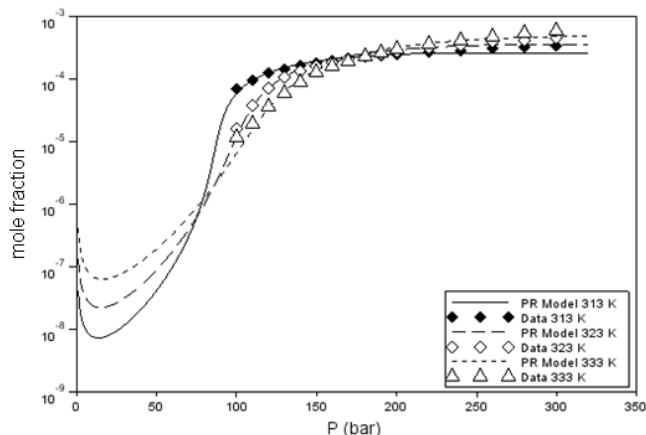
Table 1. Critical properties, boiling point and acentric factor of the characterized components for askarel oil

Property ^a	tetrachloro-biphenyl ^b	pentachloro-biphenyl ^b	hexachloro-biphenyl ^b	heptachloro-biphenyl ^b	1,2-dichloro-benzene ^c	hexachloro-benzene ^c
T_b (K)	633.15	654.15	673.15	690.15	453.57	582.55
T_m (K)	453.00	350.00	377.00	383.00	256.15	501.7
T_c (K)	875.15	892.01	906.41	918.46	705.00	825.00
P_c (bar)	27.24	25.81	24.51	23.29	40.70	28.50
ω	0.5943	0.6499	0.705	0.759	0.219	0.497
MM (g/mol)	291.99	326.43	360.82	395.24	147.003	284.782

^a T_b : normal boiling, T_m : normal melting, T_c : critical temperature, P_c : critical pressure, ω : acentric factor, MM: molecular mass.

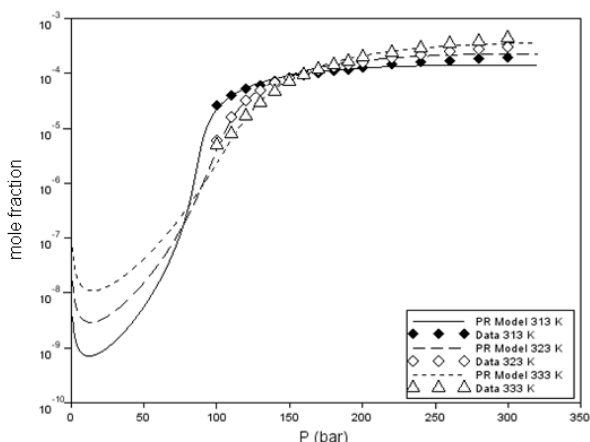
^bValues of T_b of congeners of PCB were found from the literature [27-28] and the other properties were estimated by group contribution methods [33-34]

^cValues of T_b , T_c , P_c and ω were retrieved from the AIChE DIPPR databank [40]



T (K)	313-333
k_{ij}	0.108
AARD (%)	27.95
k_{ij}	-4.244
l_{ij}	-7.053
AARD (%)	12.8
k_{ij}	0.281
l_{ij}	0.174
A	33.35
B	12191.6
AARD (%)	9.53
Data Points	45

Figure 2 - Solubility of hexachlorobiphenyl in supercritical CO₂ as function of the pressure, using the Peng-Robinson (PR). The correlation presented in the plot has 45 experimental values retrieved from Anitescu and Tavlarides [9] and the lines represent the modeling with four fitted parameters (AARD = 9.5%).



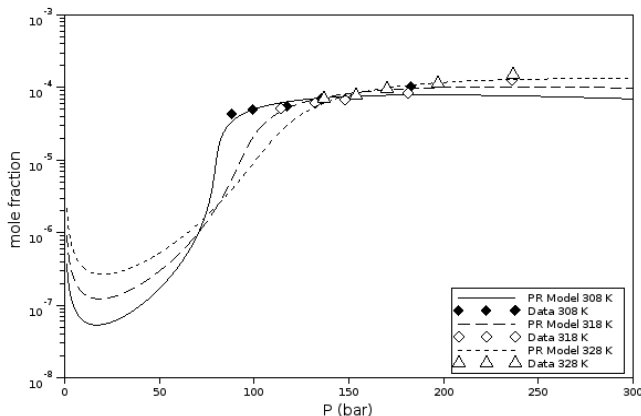
T (K)	313-333
k_{ij}	0.157
AARD (%)	26.47
k_{ij}	-3.47
l_{ij}	-5.89
AARD (%)	15.35
k_{ij}	0.258
l_{ij}	0.179
A	40.38
B	15143.8
AARD (%)	9.539
Data Points	45

Figure 3 - Solubility of heptachlorobiphenyl in supercritical CO₂ as function of the pressure, using the Peng-Robinson (PR). The correlation presented in the plot has 45 experimental values retrieved from Anitescu and Tavlarides [9] and the lines represent the modeling with four fitted parameters (AARD = 9.5%).

The last two main compounds for the askarel characterization were hexachlorobenzene and 1,2-dichlorobenzene.

Experimental data for hexachlorobenzene were digitalized from the plot of solubility versus carbon dioxide density presented by Cross and Akgerman [26]. The correlation results are reported in Figure 4, following the same performance and behavior, observed for the aromatic and PCB species. It may be easily observed the improvement gained by estimating A and B together with interaction mixing rule parameters (k_{ij} and l_{ij}) with just k_{ij} with A and B fixed and determined from vapor pressure data, i.e., 9.86 and 2203.72, respectively.

For 1,2-dichlorobenzene the situation was different due to its state of aggregation at the operational temperature range, i.e., liquid state. Therefore, the determination of interaction mixing rule parameters (k_{ij} and l_{ij}) were performed by vapor-liquid equilibrium calculation, using experimental values published by Walther and Maurer [29]. The estimated values for k_{ij} and l_{ij} were 0.084 and 0.037, respectively. Vapor pressure constants, Equation 6, were also estimated from experimental data [40] for the solubility calculation. In order to test the validity of the solubility calculation, Equation 3, with these new parameters the approach was also applied and the same type of profile was obtained. Figure 5 shows this profile along with the vapor pressure correlation performed.



T (K)	313-333
k_{ij}	0.309
A	10.42 ^a
B	3205.20 ^a
AARD (%)	34.54
k_{ij}	-0.447
l_{ij}	-0.958
A	25.67
B	8939.91
AARD (%)	9.539
Data Points	11.96

^aParameters from vapor pressure data [40]

Figure 4 - Solubility of hexachlorobenzene in supercritical CO₂ as function of the pressure, using the Peng-Robinson (PR). The correlation presented in the plot has 12 experimental values retrieved from Cross and Akgerman [26] and the lines represent the modeling with four fitted parameters (AARD = 11.96%).

A validation of the calculation procedure for a two solute system could be provided with the experimental study provided by Liu and Nagahama [41]. The determination of the solute concentrations is determined by the solution of the system of two equations at determined temperature and pressure. Figure 6 illustrates that this procedure reproduce satisfactorily the behavior of the phenanthrene solubility in the ternary mixture with the previously estimated binary interaction parameters and solute vapor pressure constants.

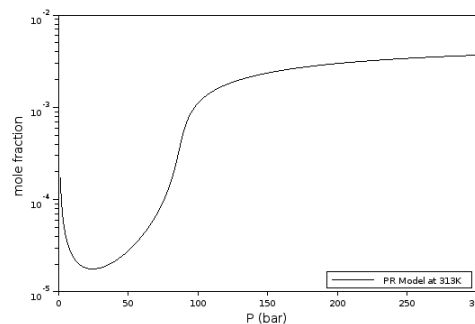
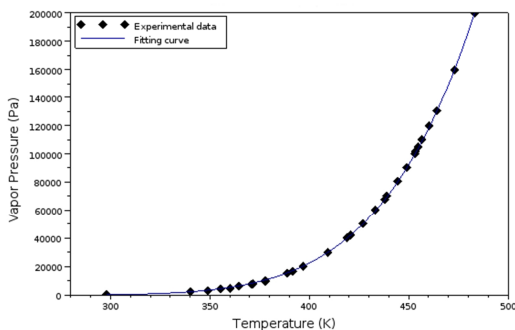
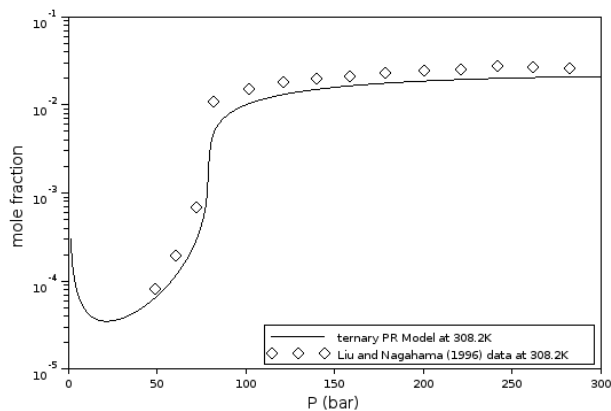


Figure 5 – Vapor pressure of 1,2-dichlorobenzene and its solubility in supercritical CO₂ as function of the pressure, using the PR EoS at 303 K, with values of k_{ij} and l_{ij} equal to 0.084 and 0.037, respectively. The vapor pressure constants, Equation 6, are: $A = 9.86$ and $B = 2203.72$



T (K)	308-328
<i>Naphthalene Parameters</i>	
k_{ij}	-0.042
l_{ij}	-0.202
A	33.84
B	9389.45
<i>Phenanthrene Parameters</i>	
k_{ij}	-0.554
l_{ij}	-1.090
A	34.81
B	11389.20

Figure 6 – Solubility of phenanthrene for the carbon dioxide + naphthalene + phenanthrene system at 308.2 K; line represents the calculated values with estimated parameters and \diamond are experimental values [41]

Using this mathematical approach, the solubility curves of askarel oil as function of operational conditions of extraction can be evaluated. Two plots are presented in Figure 7, i.e., the individual species concentrations as function of the pressure and also the profile of the askarel solubility, which is actually the summation of the solute mole fractions at 313 K. The order of magnitude and the behavior of the solubility are in agreement with the literature [42].

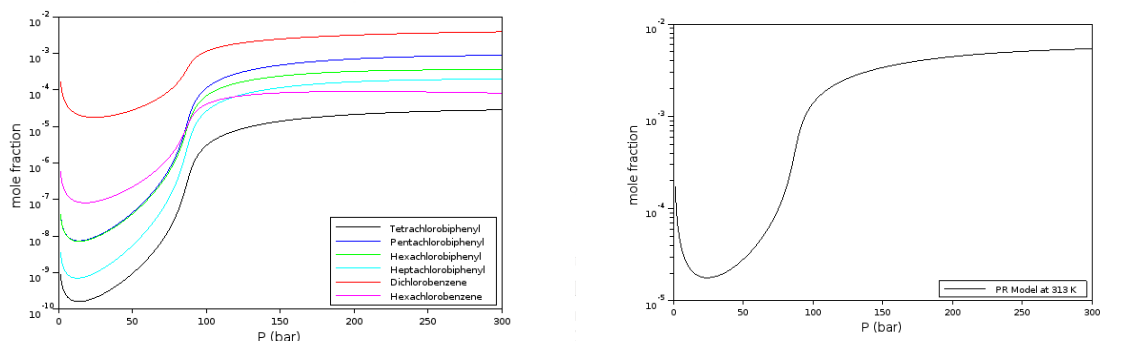


Figure 7 – Simulation results with estimated solubility model parameters for the system with tetra, penta, hexa, heptachlorobiphenyla, 1,2-dichlorobenzene and hexachlorobenzene in CO₂-SC at 313 K; Solubility of askarel, characterized by the summation of the main species considered in CO₂-SC at 313 K.

4. Conclusions

It was observed various aspects of difficulty in this calculation approach that have been faced and overcome. Solutes present very low values of solubility and vapor pressure of the compounds. By the other hand the values of fugacity coefficients are high and have to change upon independent variables, i.e., concentration, temperature and pressure. An analysis and selection of a data bank were fundamentally required. Therefore, this work required a rigorous procedure in the use of experimental information and estimations due to the sensitivity of the calculation.

Main literature source of experimental data [9] shows the application an empirical correlation of the solubility data as function of solvent density. They showed deviation results of in average 6 %, which is comparable to the proposed model (10%). However, the advantage of the proposed approach with EoS is the applicability in different operational conditions, i.e., pressure, temperature and composition, allowing the insertion of other compounds, once it is based on the principle of corresponding states.

The computational tool developed can be applied for the modeling and analysis of solubility data in supercritical fluids with flexibility, for instance, improvement or change of the EoS. The solubility model may also be applied to a desorption approach to describe phenomenologically the supercritical extraction process for operational and design purposes.

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