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Technical equation of state models for heat transfer fluids made of biphenyl and diphenyl ether and their mixtures

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ABSTRACT

Complete thermodynamic models were developed for the estimation of thermodynamic properties of biphenyl ($C_{12}H_{10}$, CAS number 92-52-4), diphenyl ether ($C_{12}H_{10}O$, CAS number 101-84-8), and of their mixtures. These compounds are used as heat transfer fluids, both in the liquid and in the vapor phase, especially in the eutectic formulation (commercially known mainly as Therminol® VP-1 and Dowtherm® A). In particular, these fluids are adopted as thermal energy carriers in concentrated solar power plants using parabolic troughs linear concentrators. The developed models are based on the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) and on the improved PRSV (iPRSV) technical equations of state (EoS), complemented by the Wong–Sandler mixing rules. The models' performance is discussed and their predictions compared with experimental data. It is proven that, from an engineering viewpoint, sufficiently accurate predictions can be obtained with both models. The model based on the PC-SAFT EoS is overall more accurate, but its mathematical complexity could play a significant role if computation time is an issue. On the other hand, the iPRSV-based model could be the solution of choice for applications requiring maximum computational efficiency such as, e.g., the process-level simulation of parabolic troughs solar collectors.

1. Introduction

This article documents the development of models for the estimation of thermodynamic properties of binary mixtures of biphenyl ($C_{12}H_{10}$, CAS number 92-52-4) and diphenyl ether ($C_{12}H_{10}O$, CAS number 101-84-8), and their evaluation related to engineering applications. Their eutectic mixture (CAS number 8004-13-5) is widely used in the industry in several fields, and it is known with the commercial names Therminol® VP-1 [1] and Dowtherm® A [2].

Biphenyl (or diphenyl or phenylbenzene or 1,1′-biphenyl or lemonene) is an aromatic hydrocarbon whose molecule consists of two connected phenyl rings, as shown in Fig. 1.

It is a colorless solid at room temperature with a distinctively pleasant smell. Biphenyl is also used as an intermediate in the production of a variety of compounds such as: emulsifiers, optical brighteners, crop protection products and plastics, dye carriers in textiles and copying paper, and solvents for pharmaceuticals. It is also used in the food industry as a preservative, known as E230. Biphenyl occurs naturally in coal tar, crude oil, and natural gas and can be isolated from these sources via distillation as shown, e.g., in Ref. [3]. The industrial production follows two main routes: (i) it is a byproduct of the dealkylation of toluene to produce benzene, (ii) it can be obtained through the oxidative dehydrogenation of benzene. The estimated worldwide production through these processes is around 40,000 metric tons [4]. According to the NFPA Hazard Classification, biphenyl is mildly toxic since, on exposure, it would cause significant irritation, but only minor residual injury, such that only breathing protection is needed [5].

Diphenyl ether (or biphenyl oxide or 1,1′-oxybisbenzene or phenoxybenzene) presents the same molecular structure of biphenyl, but with an oxygen bond connecting the phenyl rings, see Fig. 1. It is a colorless solid at room temperature with a geranium-like odor. Diphenyl ether is also used as an intermediate in the production of surfactants, and for such reactions as halogenation, acylation, and alkylation. Other applications are found in the production of polyesters and soap perfumes, while several polybromine derivatives are used as fire retardants. It is industrially produced using the direct phenol method, but is also a significant side product in the high-pressure hydrolysis of chlorobenzene in the manufacturing

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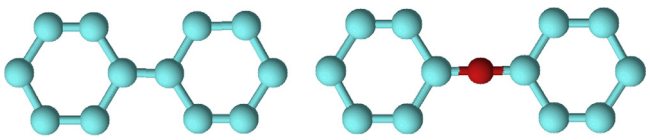

Fig. 1. Molecular structure of biphenyl (a) and diphenyl ether (b).

of phenol. The global industry capacity is estimated to be around 60,000 metric tons [6]. The NFPA Hazard Classification is equivalent to the one for biphenyl [5].

The eutectic mixture formulation of biphenyl and diphenyl ether is widely used in important industrial processes, such as in the manufacture of synthetic rubber, artificial fibers, plastics, and pigments, and in the processing of hydrocarbons (e.g. natural gas purification, asphalt processing, gas-to-liquid fuel production). This compound is also often adopted as heat transfer fluid (HTF) in large-scale concentrating solar power plants [7,8].

Notwithstanding the widespread industrial use of these compounds, no complete thermodynamic model has been developed and presented in the literature so far. Some ancillary function, like, e.g., those for the computation of vapor pressures, are the only available information, which has been used to develop the models documented here.

In order to obtain complete thermodynamic models for the two fluids and their mixtures, two different equation of state (EoS) were selected: (i) the iPRSV [9], which is a cubic equation of state (CEoS) based on an improvement of the Peng–Robinson CEoS modified by Stryjek-Vera [10], and (ii) the Perturbed-Chain Statistical Association Fluid Theory (PC-SAFT) EoS [11]. CEoS are widely adopted in scientific and engineering applications as they require few experimental data and are easily extended to mixtures. In particular, the iPRSV CEoS features accurate estimations of vapor–liquid pressures and performs sufficiently well also for thermodynamic conditions other than saturation, and for the calculation of derived thermodynamic properties, except for properties in the vapor–liquid critical point region. The PC-SAFT EoS [11] is based on statistical mechanics, and thus it incorporates information at molecular level, thus reducing the need for fluid measurement data. Because of the strong physical background, it is robust, consistent, and predictive when calculating vapor–liquid equilibria and single-phase properties of complex fluids and of mixtures in general. There are modifications to the PC-SAFT model that makes it suitable to describe properties of polar compounds. Diphenyl ether is a polar molecule, but its dipole moment (1.2 Debye) is small, well below the threshold whereby polar forces become significant with respect to van der Waals forces [12]. In addition, as a final check, the authors compared the results of predictions obtained with the PC-SAFT model to those obtained with the PCP-SAFT model [13] and differences were negligible.

The choice of developing two EoS models stems from several reasons. Firstly, this allows for a straightforward comparison and evaluation of the predictive performance in relation to experimental results. Furthermore, depending on the application at hand, it might be necessary to trade higher accuracy with computational performance. In this respect, CEoS provide a good trade-off between model simplicity and accuracy [9], and are therefore expected to be the solution of choice for general modeling purposes, and in case calculation speed is in demand. On the other hand, the PC-SAFT model offers unique capabilities, like for example the possibility of performing automated process design including fluid selection,

Table 1
Summary of selected thermodynamic data for biphenyl.

Property	Value	Uncertainty	Unit	Source
Molecular weight	154.2078		$kg\,kmol^{-1}$	[17]
Critical properties				
Temperature T_c	773	±3	K	[16]
	772.5	±2	K	[15]
Pressure p_c	3.38	±0.1	MPa	[16]
	3.38	±0.025	MPa	[15]
Volume v_c	0.497	±0.016	$m^3\,kmol^{-1}$	[16]
	0.493	±0.0047	$m^3\,kmol^{-1}$	[15]
Normal boiling point T_b	528.15	<1%	K	[18]
	528.4	±0.05	K	[19]
Acentric factor ω	0.402873		–	[20]
Dipole moment μ	0		Debye	[21]

Table 2
Summary of selected thermodynamic data for diphenyl ether.

Property	Value	Uncertainty	Unit	Source
Molecular weight	170.207		$kg\,kmol^{-1}$	[17]
Critical properties				
Temperature T_c	766.8	±0.5	K	[22]
	767	±0.01	K	[23]
Pressure p_c	3.08	<5%	MPa	[22]
	3.08	<5%	MPa	[24]
Volume v_c	0.529	<5%	$m^3\,kmol^{-1}$	[23]
	0.545	<5%	$m^3\,kmol^{-1}$	[24]
Normal boiling point T_b	523.21	<1%	K	[25]
	531.46	±0.01	K	[26]
Acentric factor ω	0.443889		–	[20]
Dipole moment μ	1.16007		Debye	[24]
	1.19005		Debye	[27]