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Prediction of Henry's Constant in Polymer Solutions using the Peng-Robinson Equation of State

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***Abstract*—**The peng-Robinson (PR), a cubic equation of state (EoS), is extended to polymers by using a single set of energy (A_1, A_2, A_3) and co-volume (b) parameters per polymer fitted to experimental volume data. Excellent results for the volumetric behavior of the 11 polymer up to 2000 bar pressure are obtained. The EoS is applied to the correlation and prediction of Henry constants in polymer solutions comprising three polymer and many nonpolar and polar solvents, including supercritical gases. The correlation achieved with two adjustable parameter is satisfactory compared with the experimental data. As a result, the present work provides a simple and useful model for the prediction of Henry's constant for polymer containing systems including those containing polar, nonpolar and supercritical fluids.

***Keywords*—**Equation of state, Henry's constant, Peng-Robinson, Polymer solution.

I. Introduction

HENRY's constant of solutes in molten polymers is an important property because the solubility of small molecules in polymers is required in the industrial processing of most polymeric material. For example, devolatilization of low molecular weight solvents, like plasticizers, unreacted monomer, or toxic additives, is essential for safety, environmental, and product quality reasons. Therefore, estimation of models is required for the developing, designing and optimizing of the processes. A number of thermodynamic models have been previously proposed and were successful in this regard. These models fall in two main categories including the activity coefficient models (ACM) and equation of state models (EoS). Some significant activity coefficient models are the classical Flory-Huggins model[1], UNIFAC-FV model[2], Entropic-FV and GK-FV model[3], MEFV model[4], Freed-FV model[5], UNIFAC-ZM model[6] and the many theoretical equation of state(EoS) such as perturbed soft chain theory (PSCT)[7], GCLF[8],GC-Flory[9],COR and PCOR[10], cubic EoS[11] have been used for polymer solutions. All of these models are limited in some ways in their applicability and usefulness. In general, although the activity coefficient models appear to have better predictive capabilities, because they are not function of pressure, their usage is restricted to low pressures and to the characterization of the liquid phase.

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Therefore, we used the EoS method to prediction of Henry's constant. The purpose of the present study is the application of Peng-Robinson (PR)[12] to the correlation and prediction of Henry's constant of solvents in industrially important polymer melts. In this work we extended the PR EoS to polymers, for the accurate description of the volumetric behavior of polymer melt liquids with an exponential function. Our objective is to obtain a simple and accurate equation that can be conveniently applied for engineering design. The rest of this paper organized as follows: first, we will present the PR EoS. Subsequently, we will use the PR EoS to describe the PVT behavior of 11 polymer melts. Then, we will show how the material parameters in the PR EoS can be determined. Finally, we will predict Henry's constant based on PR EoS with van der waals one-fluid mixing rules.

II. The PR EoS For Pure Components

The Peng-Robinson equation of state is a two parameter cubic equation of state (EoS) that can be written as:

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2} \tag{1}$$

where P is the pressure, T is the temperature, v *is* the molar volume, and R is the universal gas constant. The equation of state parameters, a and b, are the energy and co-volume parameters, respectively. For low molecular weight species (i.e. the solvents in a polymer solution), the energy and co-volume parameters are given by:

$$a = \frac{0.45724(RT_c)^2}{P_c}\alpha \tag{2}$$

$$b = \frac{0.07780RT_c}{P_c} \tag{3}$$

where T_c and P_c are the critical temperature and pressure, and α is a function of Temperature and the acentric factor , ω:

$$\alpha = [1 + m(1 - T_r^{1/2})]^2 \tag{4}$$

$$m = 0.37464 + 1.54226\omega - .26992\omega^2 \tag{5}$$

As shown by Androulakis et al.[13], Eqs (4) and (5) do not yield satisfactory vapor pressure predictions for polar and

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associating compounds. Consequently, the authors proposed a different expression for the attractive term correction:

$$\alpha = 1 + d_1 X + d_2 X^2 + d_3 X^3 \quad (6)$$

$$X = 1 - T_r^{2/3} \quad (7)$$

The parameters d_1, d_2, d_3 are estimated by fitting the pure component vapor pressure data. At supercritical temperatures, the following expression was recommended:

$$\alpha = \exp(d_1 X) \quad (8)$$

$$X = 1 - T_r^{2/3} \quad (9)$$

For polymers the EoS parameters must be obtained in a different manner because the critical properties are not known. Several methods for obtaining values for polymer EoS parameters are explained in the literatures. Louli and Tassios [14], presented a method similar to that of Kontogeorgis [15] but instead of using the polymer density at only two temperatures, the values of *a* and *b* for the polymer were fit over a wide range of *PVT* data. The polymer EoS parameters obtained in this manner resulted in predicted Henry constant that were several orders of magnitude lower than those predicted using parameters obtained from any of the other methods. Errors in liquid volumes, compared with errors using parameters obtained from other methods, were much smaller as well. In this work, co-volume parameter, b, is independent of temperature, while the energy parameter, a, is assumed to be an exponential function of temperature as follows:

$$a = MW_{polymer} \exp\left(-A_1 + \frac{A_2}{T^{A_3}}\right) \quad (10)$$

Values for A_1, A_2, A_3 and b were obtained by fitting the Peng-Robinson equation of state to experimental specific volumes correlated by the Tait equation [16]. Perhaps the most common representation of polymeric PVT data is that of Tait equation. In fact, it is not a true equation of state, but rather an isothermal compressibility model. The general form of Tait equation is:

$$V(P,T) = V(0,T)\{1 - C\ln[1 + P/B(T)]\} \quad (11)$$

where the coefficient C is usually taken to be a universal constant equal 0.0894(only for PDMS polymer is 0.100916). The zero-pressure isotherm V (0, T) is usually given by:

$$V(0,T) = V_0 \exp(\alpha T) \quad (12)$$

where α is the thermal expansion coefficient. The Tait parameter B(T) is usually given by:

$$B(T) = B_0 \exp(-B_1 T) \quad (13)$$

Thus, the Tait equation is normally a four-parameter (V_0, α, B_0, B_1) representation of the experimental PVT data. In some cases, Eqs.(12) and (13) do not fit the data accurately, and polynomial expressions are used:

$$V(0,T) = \alpha_0 + \alpha_1 T + \alpha_2 T^2 \quad (14)$$

$$B(T) = b_0 + b_1 T + b_2 T^2 \quad (15)$$

Recently, a number of isothermal equations of state for solid and liquid polymers was introduced that their presenters showed the Tait equation as an approximate solution in their formulation. Summary of PVT data for 11 Homopolymer liquids that used in this study are shown in Table 1. Also, the Tait equation parameters for these 11 polymer liquids are shown in Table 2.

TABLE I
SUMMARY OF PVT DATA FOR 11 HOMOPOLYMER LIQUIDS OVER AN EXTENSIVE RANGE OF TEMPERATURE AND PRESSURE

Polymer	Symbol	Average MW	Range of data (T, ^{0}C)	Range of data (P, bar)
High density polyethylene	HDPE	105000	140-203	1-1960
Low density polyethylene	LDPE	16600	121-175	1-1960
Polystyrene	PS	110000	115-196	1-2000
Poly(vinyl acetate)	PVAc	49000	35-100	1-800
Poly(dimethylsiloxane)	PDMS	30000	25-70	1-1000
Poly(ethylene terephthalate)	PET	15500	274-342	1-1960
i-polypropylene	i-PP	94100	170-297	1-1960
a-polypropylene	a-PP	94100	80-120	1-1000
Poly(vinyl choloride)	PVC	46800	100-150	1-2000
Poly(methyl methacrylate)	PMMA	75000	114-159	1-2000
Poly(tetrafluoroethylene)	PTFE	50000	330-372	1-390

TABLE II
TAIT EQUATION PARAMETERS FOR 11 POLYMER LIQUIDS

Polymer	V(P,T)=V(0,T)*{1-C(ln(1+P/B(T)))} V(0,T),cm^3/g	B(T),bar
HDPE	$1.1595 + 8.0394\times10^{-4}T$	$11799\times\exp(-4.739\times10^{-3}T)$
LDPE	$1.1944 + 2.841\times10^{-4}T + 1.872\times10^{-6}T^2$	$2022\times\exp(-5.243\times10^{-3}T)$
PS	$0.9287\times\exp(5.131\times10^{-4}T)$	$2196\times\exp(-3.319\times10^{-3}T)$
PVAc	$0.82496 + 5.82\times10^{-4}T + 2.94\times10^{-7}T^2$	$2049\times\exp(-4.346\times10^{-3}T)$
PDMS	$(0.9919 - 8.925\times10^{-4}T + 2.65\times10^{-7}T^2 - 3.0\times10^{-11}T^3)^{-1}$	$1041\times\exp(-5.851\times10^{-3}T)$
PET	$0.6883 + 5.9\times10^{-4}T$	$3697\times\exp(-4.15\times10^{-3}T)$
i-PP	$1.1606\times\exp(6.7\times10^{-4}T)$	$1491\times\exp(-4.177\times10^{-3}T)$
a-PP	$1.1841 - 1.091\times10^{-4}T + 5.286\times10^{-6}T^2$	$1621\times\exp(-6.604\times10^{-3}T)$
PVC	$0.7196 + 5.581\times10^{-5}T + 1.468\times10^{-6}T^2$	$2942\times\exp(-5.321\times10^{-3}T)$
PMMA	$0.8254 + 2.8383\times10^{-4}T + 7.792\times10^{-7}T^2$	$2875\times\exp(-4.146\times10^{-3}T)$
PTFE	$0.32 + 9.5862\times10^{-4}T$	$4252\times\exp(-9.38\times10^{-3}T)$

The regression was accomplished by using the optimization program. Values A_1, A_2, A_3, and b are determined by minimizing the following function:

$$F = \frac{1}{n}\sum_n \left(\frac{\left|1/V_{calc} - 1/V_{exp}\right|}{1/V_{exp}}\right) \quad (16)$$

where V_{calc} and V_{exp} are obtained volume of PR EoS and Tait equation in every iteration, respectively. The obtained values

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of the PR EoS parameter and the absolute average deviation for 11 polymer liquids in this work are comprised in Table3.

TABLE III
EQUATION OF STATE PROPERTIES FOR 11 POLYMER LIQUIDS USING THE METHOD PROPOSED IN THIS STUDY

Polymer	b/MW,	A_1	A_2	$A_3/10^{-3}$	% AAD[a]
HDPE	1.0546	2.1343	22.8957	3.759	0.36
LDPE	1.0554	1.6347	20.8624	6.679	0.41
PS	0.8396	0.9714	21.4350	2.5681	0.23
PVAc	0.7442	0.3918	22.2256	22.252	0.08
PDMS	0.8586	1.6460	21.3042	9.848	0.21
PET	0.6888	1.1243	21.4601	1.995	0.23
i-PP	1.0650	0.1536	21.4889	8.859	0.59
a-PP	1.0213	0.1177	21.5516	11.360	0.18
PVC	0.6244	1.1542	20.5060	3.702	0.13
PMMA	0.7430	1.1828	21.8362	7.860	0.16
PTFE	0.4044	3.3845	22.2860	3.407	0.49

[a] Average absolute deviation is defined as $(100/N)\sum(|V_{calc}-V_{\exp}|/V_{\exp})$ where V_{calc} and V_{exp} refer to calculated and experimental equilibrium volume, respectively. N denotes the number of experimental data points (100 points for all polymers in this study).

According to Table3, the average absolute deviation between the experimental and calculated volume is below 0.6 percent. So, the proposed relationship for energy parameter, a, can use to satisfactory express the behavior of this polymers liquids over the specified temperature and pressure. Typically, Figs1 to 3 show the V-P diagrams for polymers PVAc, PMMA and PS.

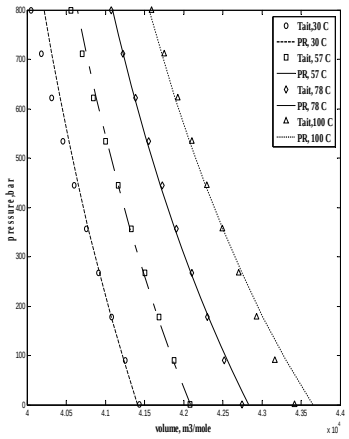


Fig. 1 V-P diagram for PVAc. Symbols and solid line curves stand for the experimental points and the calculated values respectively

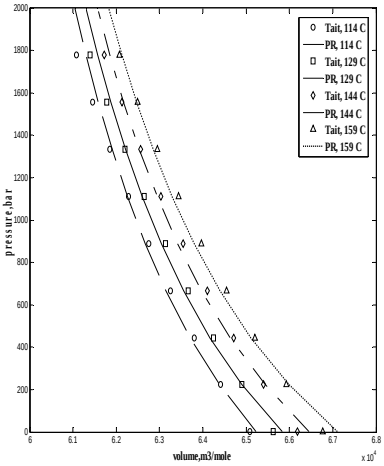


Fig. 2 V-P diagram for PMMA. Symbols and solid line curves stand for the experimental points and the calculated values respectively

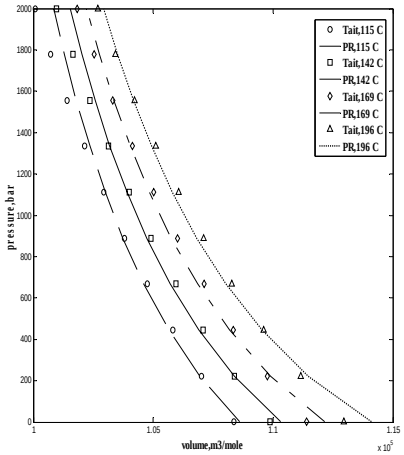


Fig. 3 V-P diagram for PS. Symbols and solid line curves stand for the experimental points and the calculated values respectively.

III. EXTENSION OF PR TO POLYMER/SOLVENT MIXTURE

For extension of the PR equation of state to mixtures containing both solvents and polymers, we adopt the van der waals one-fluid mixing rule:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{17}$$

$$b_m = \sum_i x_i b_i \tag{18}$$

where:

$$a_{ij} = (1 - L_{ij})(a_i a_j)^{1/2} \tag{19}$$

As expected, L_{ij} is a function of temperature, then we suggested a linear dependence of $(1-L_{ij})$ on temperature as shown in Eq (20).Thus, a two parameter correlation is possible based on the follow equation:

$$1 - L_{ij} = l_{ij,0} T + l_{ij,1} \tag{20}$$

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In the above equations, x_i denotes the mole fraction of component i. a_i and b_i refer to the EoS parameters for each species in the mixture and l_{ij} is the binary interaction parameter.

Based on the definition of Henry's constants [17] and using the above mixing rules, we obtain the following expression for the Henry's constant of a solvent in a polymer at a temperature T:

$$H_{12}=\lim_{x_1\to\infty}\varphi_1 P=\exp(\ldots)\frac{b_1}{b_2}\frac{RT}{V_2-b_2}\left(\frac{V_2+b_2-b_2\sqrt{2}}{V_2+b_2+b_2\sqrt{2}}\right)^{\left(\frac{a_{12}}{RTb_2\sqrt{2}}\right)} \quad (21)$$

With subscript 1 corresponding to the solvent and 2 to the polymer, and φ_1 is the fugacity coefficient of the solvent in the mixture calculated from the PR EoS. Notice that H_{12} from equation is the molar fraction based Henry's constant. The relation between this quantity and the one usually reported in experimental studies, the weight fraction based Henry's constant, can be shown to have the following form:

$$H_{12}^{\omega}=H_{12}\left(\frac{M_2}{M_1}\right) \quad (22)$$

where M_1 is the molecular weight of the solvent and M_2 the molecular weight of the polymer.

IV. Results And Discussion

Henry's constant calculations are carried out for three polymers PVAc, LDPE and PS with a variety of solvents by using Eq. (21) by adjusting the value of the interaction parameter $l_{ij,0}$ and $l_{ij,1}$ for each polymer/solvent mixture. The results for the weight fraction based Henry's constants obtained from this two parameter correlation, are shown in Figs.4 to 6 and the interaction parameters and AAD for each polymer solution is shown in Table4. The following comments summarize our observations on the obtained results.

1. Excellent results for the volumetric behavior of the 11 polymer up to 2000 bar pressure are obtained. The ability of the PR EoS to prediction of PVT behavior of polymer melts –pure was confirmed through the tables and figures presented in this work.
2. Very satisfactory results are obtained between calculated and experimental Henry constants with the average error for each polymer/solvent system generally being less than 3%.

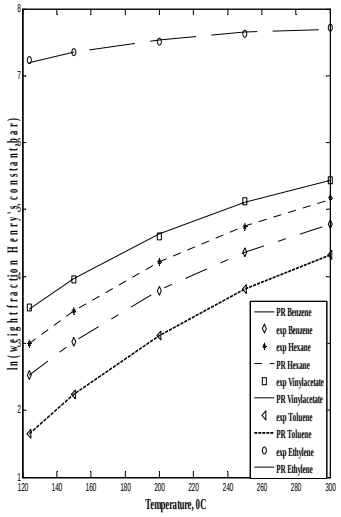


Fig. 4 Experimental [18] and Calculated weight fraction Henry's constants vs. temperature for LDPE with the PR EoS

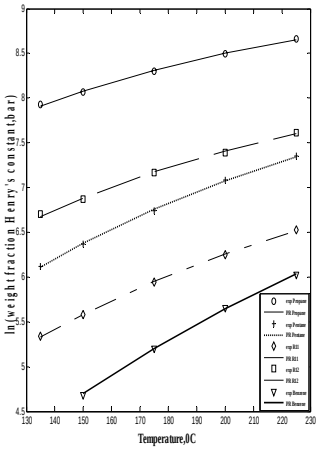


Fig. 5 Experimental [19] and Calculated weight fraction Henry's constants vs. temperature for PS with the PR EoS

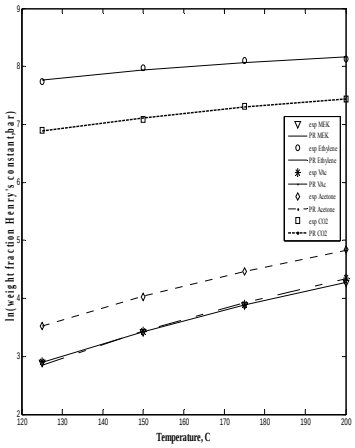


Fig. 6 Experimental [20] and Calculated weight fraction Henry's constants vs. temperature for PVAc with the PR EoS

TABLE IV
PARAMETERS VALUES FOR L_{ij} BASED ON THE PR EOS FOR THE PREDICTION OF HENRY'S CONSTANT

Polymer	Solvent	$L_{ij,0}$	$L_{ij,1}$	% AAD
LDPE	Benzene	-3.89e-4	0.9041	0.44
	Ethylene	-1.07e-3	0.8177	2.30
	Toluene	-3.14e-4	0.9356	0.60
	Vinyl acetate	-2.77e-4	0.8310	1.90
	Hexane	-2.13e-4	0.9712	0.92
PS	Benzene	-7.35e-4	0.8831	0.67
	Pentane	-7.55e-4	0.9418	0.82
	Propane	-1.28e-3	0.8461	1.11
	R11	-9.71e-4	0.8919	0.80
	R12	-1.37e-4	0.8848	1.11
PVAc	Acetone	-4.28e-4	0.9354	0.36
	Ethylene	-1.36e-3	0.9198	2.60
	Co_2	-1.58e-3	0.8906	1.16
	Methyl ethyl ketone	-1.79e-4	0.9551	0.60
	Vinyl acetate	-1.97e-4	0.9533	1.80

V. CONCLUSION

A cubic EoS, in this case the PR , is applied to the prediction of Henry's constant for polymer-solvent systems. Polymer EoS parameter, A_1, A_2, A_3 and b are determined by fitting polymer PVT data and provides excellent results to description of the pure polymer behavior up to high pressures. Prediction of Henry's constants for a variety of nonpolar and polar systems is carried out by using vdw1f mixing rule. Satisfactory description of Henry's constant data is obtained with the error <3% by allowing the interaction parameter l_{12} to become a linear function of temperature. As a result, this work presents a simple and useful model for the prediction of Henry's constant for polymer systems.

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