

GAS SOLUBILITY AT HIGH PRESSURES IN POLYMER SOLUTIONS USING THE SAFT-VR EQUATION OF STATE

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ABSTRACT

Gas solubility is important for the material processing, food packaging and fundamental study of the diffusion process. The SAFT-VR equation of state is employed in this study to calculate the gas solubility of supercritical gases in various polymer substrates. Regressions of the equation of state parameters for pure polymers are presented with satisfactory results. Solubilities of supercritical carbon dioxide, nitrogen, ethane and propane in various polymer solutions are calculated using simple mixing rules. It is shown that this equation of state is satisfactory for gas solubility calculations on polymer and copolymer systems.

INTRODUCTION

Polymer materials are important for industrial applications, and the knowledge of phase equilibrium or solvent solubility for polymer systems is essential for a feasible chemical process design. Various methods have been applied to determine the gas solubility at high pressures into molten polymers, for example the perturbed hard chain theory [1], the lattice-fluid equations of state (EOS) [2, 3]. In recent literature, Zhong and Masuoka [4] applied the Peng-Robinson EOS to model the gas solubility in polymers with absolute average deviation (AAD) about 10%. Hamedi et al. [5] applied the group-contribution lattice-fluid EOS to predict the solubility of carbon dioxide in polymers with an AAD of 25%.

The SAFT-VR (Statistical Associating Fluid Theory, Variable Range) EOS is a recently developed equation for fluids and mixtures from small molecules to strongly associating fluids and polymers [6]. It appears as an improved version of the original SAFT EOS and shows greater flexibility on phase equilibrium calculations. In this study, the SAFT-VR EOS is employed for supercritical gas solubility calculations on polymer solutions. New SAFT-VR EOS parameters are presented and the gas solubility calculation results are compared with those from previous models.

METHOD OF CALCULATION

The SAFT-VR EOS for non-associating systems is represented by:

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{mono}}{NkT} + \frac{A^{chain}}{NkT} \quad (1)$$

where A is the Helmholtz free energy, and is divided into three contributions from ideal gas, monomer segment and chain interactions. The detail expressions for each term in the SAFT-VR EOS are shown in literature [6]. For each pure fluid, there are four EOS parameters: the segment number m , size parameter σ , energy parameter ε/k_B (k_B , the Boltzmann constant), and a range of interaction parameter λ . For many polymers, these parameters are not available in literature and are regressed using experimental density data in this study. Gas solubility calculations are then carried out solving the phase equilibrium equations for temperature, pressure and chemical potentials, respectively. For polymers with low vapor pressures, it is convenient to assume there is no polymer molecule in the gas phase. The mixing rules used in this study are:

$$\sigma_{ij} = 0.5(\sigma_i + \sigma_j) \quad (2)$$

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{0.5} (1 - k_{ij}) \quad (3)$$

$$\lambda_{ij} = \frac{\lambda_i \sigma_i + \lambda_j \sigma_j}{\sigma_i + \sigma_j} \quad (4)$$

where k_{ij} is a binary interaction parameter determined by minimizing the calculated error of gas solubility in polymer solutions.

RESULTS AND DISCUSSION

Table 1 presents the pure polymer parameters of the SAFT-VR EOS. The liquid molar volumes are satisfactorily correlated using this EOS in a large temperature and pressure range. A typical result is shown graphically in Fig.1 for a co-polymer. Gas solubility calculation results are shown in Table 2. The binary interaction parameters are either taken as a constant or temperature-dependent for each system. The grand average deviation of the SAFT-VR EOS is around 6%. A typical result is also shown in Fig. 2. We have compared our calculation results with those from the Sanchez-Lacombe (SL) EOS [2] and the Panayiotou-Vera (PV) EOS [3] with their originally reported pure fluid parameters and the best-fitted binary interaction constants. Six systems and 115 data points with supercritical carbon dioxide and nitrogen are investigated. Generally, the SAFT-VR and SL EOS yields comparable accuracy where the calculated error for gas solubility in polymer solution is 8.5%. The PV EOS shows an error about 12%. The binary parameters for the SAFT-VR EOS are in a relatively narrower range. This favors engineering applications of the SAFT-VR EOS.

CONCLUSION

The SAFT-VR EOS is satisfactorily employed for the calculations of solubility of supercritical gases in polymer solutions. The binary interaction parameters are relatively in a narrower range and this makes the SAFT-VR EOS more suitable for practical design.

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Table 1 Regressed parameters and calculated results for the systems of pure polymers using the SAFT-VR EOS

Polymer	MW (g/mol)	T (K)	P (MPa)	Data Pts	m/MW	σ (Å)	ϵ/k_B (K)	λ	AAD (%)
LDPE	600,000	413.15-473.15	0.1-100	44	0.0240	4.1246	343.9873	1.5732	0.07
HDPE	52,000	413.15-473.15	0.1-196	52	0.0136	5.1600	518.5592	1.4508	0.10
PS	279,000	388.55-468.75	0.1-200	69	0.0142	4.7229	426.9575	1.8071	0.14
PP	570,000	503.15-563.15	0.1-200	52	0.0141	5.0474	451.5047	1.4629	0.10
PB	1,800,000	423.15-513.15	0.1-200	52	0.0148	4.9626	469.7971	1.4489	0.10
PVAC	330,000	308.15-373.15	0.1-80	110	0.0240	3.6844	296.9630	1.7180	0.03
PMMA	100,000	386.65-432.15	0.1-200	41	0.0251	3.6168	339.9704	1.6557	0.08
PBMA	100,000	295.15-472.65	0.1-200	168	0.0203	4.1119	400.2573	1.5039	0.19
PCHMA	100,000	382.75-472.05	0.1-200	90	0.0180	4.2000	427.5870	1.5410	0.12
PC	60,000	423.8-603.4	0.1-200	57	0.0160	4.2784	496.6316	1.4382	0.08
ICP-PP	240,000	453.8-573.4	0.1-200	49	0.0103	5.8022	613.3639	1.3226	0.10
PIB	36,000	325.95-383.15	0.1-100	55	0.0157	4.7661	499.3096	1.6845	0.06
PDMS	166,000	298.05-343.05	0.1-100	66	0.0167	4.4301	315.3462	1.4775	0.05
PBD	100,000	277.15-328.15	0.1-250	84	0.0165	4.7936	489.2773	1.7986	0.07
PPO	47,000	489.15-593.15	0.1-170	75	0.0222	3.8277	350.9961	1.5303	0.08

Table 2 Calculated results of gas solubility for the binary systems of gas (1) + polymer (2) using the SAFT-VR model

Binary systems	Temp. range (K)	Pressure range (MPa)	Data pts	AAD (%)	
				T-independent k_{12}	T-dependent k_{12}
CO ₂ + PS	373.2-453.2	2.47-20.04	26	5.77	4.41
CO ₂ + PP	433.2-473.2	5.42-17.53	20	9.54	9.37
CO ₂ + HDPE	433.2-473.2	6.61-18.12	17	8.37	8.20
CO ₂ + PVAC	313.15-373.15	0.20-17.45	31	4.04	2.46
CO ₂ + PMMA	398.15-473.15	0.1-2.0	41	2.22	0.81
CO ₂ + PBMA	313.2-353.2	0.55-10.20	63	9.45	4.38
CO ₂ + PPO (L)	373.15-473.15	2.10-19.96	19	8.18	5.27
CO ₂ + PPO (H)	373.15-473.15	1.98-20.21	30	8.31	8.22
CO ₂ + PIB	461.48	0.10-2.03	12	NA	0.25
CO ₂ + PBD	298	0.1-4.5	10	NA	3.88
CO ₂ + PDMS	298	0.1-4.5	10	NA	7.21
N ₂ + PS	373.2-453.2	6.45-18.01	18	14.14	2.40
N ₂ + PP	453.2-473.2	4.01-18.0	14	7.74	3.07
N ₂ + HDPE	433.2-473.2	2.54-15.21	20	6.38	2.32
C ₂ H ₄ + ICP-PP	323.2-363.2	0.37-3.04	18	1.84	0.56
C ₃ H ₆ + PP	323.2-363.2	323.2-363.2	27	4.70	4.02
C ₃ H ₆ + ICP-PP	323.2-363.2	323.2-363.2	18	6.71	5.91
Grand			394	6.27	4.18

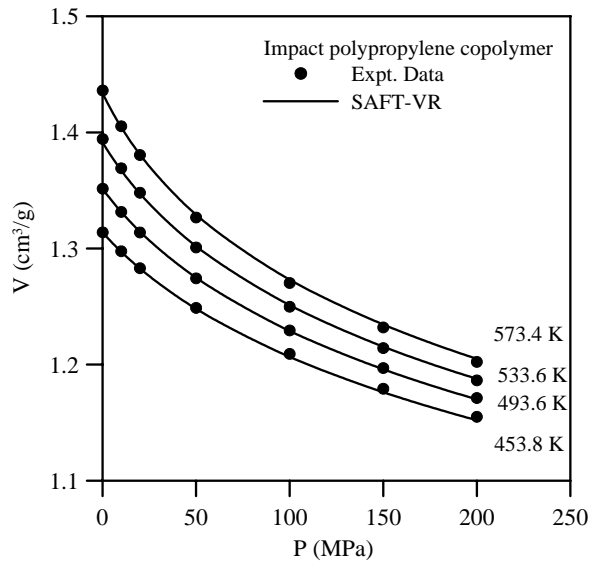


Fig. 1 Comparison of the experimental data and calculated liquid volume of copolymer ICP-PP using the SAFT-VR model

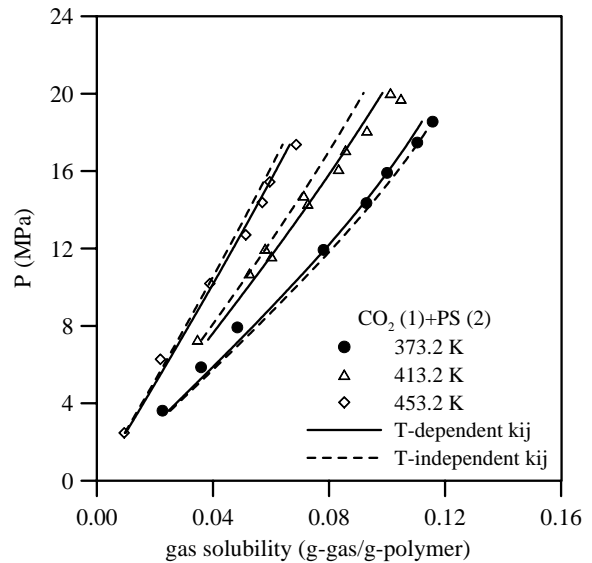


Fig. 2 Comparison of the calculated gas solubility using T- independent k_{12} and T-dependent k_{12} for the system of CO₂+PS