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Predicting Specific Volumes of Pure Polymers and VLE of Polymer Solutions by Group-Contribution Lattice Theory[1]

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A generalized group-contribution (GC) scheme with an equation of state (EOS) presented previously by the present authors was extended to the prediction of specific volumes of pure polymers and vapor-liquid equilibria of polymer solutions. The GC-EOS requires only two parameters, representing group size and interaction between groups. A unique feature of the approach is that a single set of group information can be applied to predict both the configurational properties of pure polymers and mixtures in general. The approach was illustratively applied to the prediction of the density of pure polymers, vapor pressures of organic solvents, and phase equilibria of their polymer solutions.

KEY WORDS: lattice-hole theory; polymer solutions, specific volume, vapor-liquid equilibria.

1. INTRODUCTION

Polymeric process design requires estimation of phase equilibrium data. While the estimation can often be made from experimental data, in many cases experimental data are severely limited. When no experimental data are available, design engineers can do little more than make a reasonable guess, often with large uncertainty. Toward reducing the uncertainty, this

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work provides a new rational frame of group contribution (GC) for predicting configurational properties of pure polymers and solutions in general.

Historically, the GC approach has been applied separately to pure properties [1, 2] and to excess properties of mixtures [3]. However, no GC formulation has been made to predict both the pure properties and the phase equilibria of mixtures of real fluids, although partial success has been accomplished [4]. Recently, the present authors formulated a generalized GC scheme which is applicable to both pure fluids and mixtures, and it was applied successfully to low molecular hydrocarbon systems [5–7]. This work is an extension and further revision of the previous work for predicting macromolecular configurational properties.

2. GROUP-CONTRIBUTION METHOD

As presented elsewhere by the present authors [8], the equation of state (EOS) extended to GC was based on the lattice-hole theory of r-mers and it requires only two parameters, representing the molecular segment size r_i and interaction energy ε_{ij} for a pure fluid, and an adjustable interaction energy parameter, λ_{ij}, in the combination rule $\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{0.5}(1-\lambda_{ij})$. The present GC approach was intended to represent the molecular parameters r_i and ε_{ij} in terms of r_i^{G} and $\varepsilon_{ij}^{\mathrm{G}}$ without employing λ_{ij} by the formulations,

$$r_i = \sum_{j=1}^{g} \nu_{ij} r_j^{\mathrm{G}} \tag{1}$$

$$\varepsilon_{ij} = \sum_{k=1}^{g} \sum_{l=1}^{g} \theta_{ik}^{\mathrm{G}} \theta_{jl}^{\mathrm{G}} \varepsilon_{kl}^{\mathrm{G}} = \sum_{k=1}^{g} \sum_{j=1}^{g} \nu_{ik} \nu_{jl} q_k^{\mathrm{G}} q_l^{\mathrm{G}} \varepsilon_{kl}^{\mathrm{G}} \Big/ \sum_{k=1}^{g} \sum_{j=1}^{g} \nu_{ik} \nu_{jl} q_k^{\mathrm{G}} q_l^{\mathrm{G}} \tag{2}$$

where ν_{ij} is the number of group j in species i and θ_{ik}^{G} is the surface area fraction of group k in species i. These relations [Eqs. (1) and (2)] imply that the group interactions should be identical for groups either in pure fluids or in mixtures [9]. Since the effect of the molecular bulkness factor is not significant, we set $q_j^{\mathrm{G}} = r_j^{\mathrm{G}}$ to avoid the complexity associated with the bulkness factor [10].

Temperature dependences of these parameters were represented by

$$r_j^{\mathrm{G}} = w_j^{\mathrm{G}} + h_j^{\mathrm{G}}(T - T_0) + c_j^{\mathrm{G}}\left(T \ln \frac{T_0}{T} + T - T_0\right) \tag{3}$$

$$\varepsilon_{ij}^{\mathrm{G}}/k = a_{ij}^{\mathrm{G}} + b_{ij}^{\mathrm{G}}(T - T_0) + d_{ij}^{\mathrm{G}}\left(T \ln \frac{T_0}{T} + T - T_0\right), \tag{4}$$

where T_0 is an arbitrarily chosen reference temperature (298.15 K). The numerical parameters were determined from pVT and vapor pressure data of pure substances and phase equilibrium data for polymer solutions [3, 11, 12].

3. MODEL EQUATION OF STATE

As discussed previously by the present authors [8], the volumetric EOS based on approximate lattice-hole theory was written as

$$P=\left(\frac{1}{\beta V_{\mathrm{H}}}\right)\left\{\left(\frac{z}{2}\right)\ln\left[1+\left(\frac{q_{\mathrm{M}}}{r_{\mathrm{n}}}-1\right)\rho\right]-\ln(1-\rho)\right\}-\left(\frac{z}{2}\right)\theta^2\left(\frac{\varepsilon_{\mathrm{M}}}{V_{\mathrm{H}}}\right) \tag{5}$$

$$\varepsilon_{\mathrm{M}}=\left(\frac{1}{\theta^2}\right)\left[\sum\sum\theta_i\theta_j\varepsilon_{ij}+\left(\frac{\beta}{2}\right)\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij}+3\varepsilon_{kl}-2\varepsilon_{ik}-2\varepsilon_{jk})\right] \tag{6}$$

Table I. Coefficients in the Temperature-Dependent Segment Number Correlation Given by Eq. (3)

Group	w_j^{G}	h_j^{G}	c_j^{G}	Temperature range (K)
CH_3	2.654657	0.000203	−0.001786	270–450
CH_2	1.539918	−0.000201	0.001218	270–450
CH	0.453506	−0.002425	−0.000593	270–450
C=C	0.206991	−0.002412	0.001287	270–450
OH	1.479771	0.004273	0.006132	270–450
CH_3OH	3.969967	0.004196	0.001944	270–450
$ACCH_3$[a]	2.975477	0.000146	0.001625	270–450
$ACCH_2$	1.860091	−0.000405	−0.000372	270–450
ACCH	0.708285	−0.001187	−0.001252	270–450
ACH	1.400666	0.000188	0.001062	270–450
AC	0.304028	0.000102	−0.001175	270–450
ACOH	1.732338	0.001856	0.001721	270–450
O	0.681542	0.000024	0.001242	270–450
COO	2.283009	0.001395	0.001826	270–450
CO	1.377142	0.001917	0.001526	270–450
CHO	2.285444	0.003997	−0.001847	270–450
CO_2	3.782112	0.004755	0.004512	270–450
$CYCH_2$[b]	1.651529	−0.000004	0.001141	270–450
H_2O	1.723942	0.001703	−0.001214	270–450
COOH	2.885232	0.004004	−0.000105	270–450
HCOOH	3.838395	0.003448	−0.000530	270–450
NH_2	1.778541	0.002287	0.002224	270–450

[a] AC denotes aromatic carbons

[b] CY denotes cyclic carbon.

Table II. Coefficients in the Temperature-Dependent Group–Group Interaction Parameter Given by Eq. (3)

Group–group	a_{ij}^{G}	b_{ij}^{G}	d_{ij}^{G}	Temperature range (K)
CH_3–ACH	97.353685	0.008643	−0.060582	270–450
CH_2–ACH	114.758136	0.014895	−0.035282	270–450
CH_3–CH_3	78.174322	0.050459	0.388018	270–450
CH_3–CH_2	96.049727	0.011347	−0.273514	270–450
CH_2–CH_2	112.776346	0.049733	0.070320	270–450
CH_3–OH	104.468439	−0.230105	−0.061635	270–450
CH_2–OH	204.269390	−0.707174	−1.513694	270–450
CH_3–$ACCH_3$	86.120092	0.062346	0.261681	270–450
CH_2–$ACCH_3$	121.178069	0.036096	−0.188767	270–450
CH_3–$CYCH_2$	92.543871	0.023077	−0.009809	270–450
CH_2–$CYCH_2$	112.141917	0.024503	−0.03193	270–450
ON–OH	756.626408	−4.031045	−8.787254	270–450
OH–$CYCH_2$	168.824262	−0.550121	−1.058787	270–450
ACH–ACH	119.958040	−0.011889	−0.104178	270–450
O_2–ACH	93.858901	−0.060056	−0.232417	270–450
CO_2–$ACCH_3$	84.697966	−0.023877	−0.109467	270–450
CO_2–CH_3	73.676809	−0.031117	−0.148915	270–450
CO_2–CH_2	89.951468	−0.030277	−0.144229	270–450
CO_2–CO_2	84.919753	−0.099498	−0.345484	270–450
CO_2–O	166.692163	0.010909	−0.187872	270–450
CO_2–COO	168.152075	−0.045824	0.003032	270–450
CO_2–OH	170.711031	−0.661109	−1.526007	270–450
CO_2–$CYCH_2$	86.803685	−0.044611	−0.206195	270–450
$CYCH_2$–$CYCH_2$	109.776120	0.017053	−0.074970	270–450
ACH–$CYCH_2$	112.928655	0.003416	−0.086161	270–450
ACH–$ACCH_3$	117.763895	0.012471	−0.077352	270–450
$ACCH_3$–$ACCH_3$	113.004523	0.039160	−0.001303	270–450
H_2O–H_2O	431.342973	−1.003208	−0.949707	270–450
CH_3–H_2O	367.296486	−0.631019	−0.459730	270–450
CH_2–H_2O	214.438594	−0.255987	−0.379200	270–450
OH–H_2O	142.914512	−0.276419	−0.113551	270–450
CH_3–CO	142.569937	−0.223408	−0.406103	270–450
CH_2CO	178.078211	−0.143040	0.130141	270–450
CO–CO	612.056821	−0.784793	−2.063104	270–450
CO–$CYCH_2$	170.248161	−0.168759	−0.224325	270–450
CO–ACH	222.070846	−0.276376	−0.289429	270–450
CO–$ACCH_3$	166.179368	−0.117862	−0.492145	270–450
CH_3–O	118.367350	0.376864	−0.363035	270–450
CH_2–O	112.112143	−0.416189	−0.002884	270–450

Table II. *(Continued)*

Group-group	a_{ij}^{G}	b_{ij}^{G}	d_{ij}^{G}	Temperature range (K)
O-O	365.605057	−0.547655	0.837675	270–450
O-H_2O	382.392557	−1.064526	0.500736	270–450
O-ACH	149.472686	−0.426391	0.028655	270–450
O-$ACCH_3$	148.352767	−0.264399	−0.895854	270–450
COO-CH_3	134.587601	−0.120881	−0.397246	270–450
COO-CH_2	116.981198	0.094403	0.506506	270–450
COO-COO	288.027707	−0.330029	−1.333105	270–450
COO-$CYCH_2$	136.921927	−0.075989	−0.211773	270–450
COO-ACH	173.249959	−0.106724	−0.300054	270–450
COO-$ACCH_3$	131.362051	−0.010039	−0.131480	270–450
ACH-AC	235.301862	0.372611	1.348596	270–450
AC-AC	176.972767	0.997243	3.678574	270–450
CH_3-AC	115.609139	0.530116	4.362101	270–450
CO_2-AC	161.580099	0.136410	0.541915	270–450
CH_3-CH	134.869056	0.102300	−2.594836	270–450
CH_2-CH	145.070365	0.267519	0.000830	270–450
CH-CH	213.483481	0.167150	−9,080826	270–450
CH-CO	194.285759	0.045443	−5.032975	270–450
CH-COO	138.474959	6.252771	7.979311	270–450
CH-ACH	142.028271	0.712032	−3.977048	270–450
CH-O	36.077033	0.100931	0.001103	270–450
CH_3-ACCH	196.028922	0.149379	−0.536435	270–450
CH_2-ACCH	75.205071	1.548653	3.175087	270–450
ACH-ACCH	156.011952	0.400333	−0.043588	270–450
ACCH-ACCH	968.884509	−1.422192	−8.572214	270–450
ACCH-$CYCH_2$	153.713257	0.414900	0.165263	270–450
ACCH-$ACCH_3$	168.196020	0.465003	0.725343	270–450

[a] AC denotes aromatic carbons

[b] CY denotes cyclic carbon.

where $q_M = \sum x_i q_i$ and $r_M = \sum x_i r_i$. Summations are over all molecular species unless otherwise specified.

Other thermodynamic functions such as chemical potential were omitted here [8]. By setting the coordination number $z = 10$ and unit lattice cell volume $N_A V_H = 9.75\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, where N_A is Avogadro's number, one needs to determine two molecular parameters, r_i and ε_{ij}, in terms of group information as given by Eqs. (3) and (4). Determined values of group information are summarized in Tables I and II.

4. APPLICATION TO REAL FLUIDS

4.1. Prediction of Vapor Pressures and Specific Volumes

Since the quantitative prediction of vapor pressures of low molecular hydrocarbon solvents was demonstrated previously elsewhere [5–7], we omit further discussion of that here. In Fig. 1, the predicted and experimental specific volumes [13] of high-density poly(ethylene) at 434.15, 454.15, and 477.15 K are compared. Up to 200 MPa the GC-EOS predicts the specific volumes reasonably well. Also, in Fig. 2, the predicted specific volumes of low-density poly(ethylene) [13] are shown. Next, the predicted and experimental [144 specific volumes of poly(*o*-methylstyrene) at 422.15 to 460.15 K and 0.1 to 200 MPa are shown in Fig. 3. Finally, the predicted specific volumes of poly(styrene: $M_n = 90, 700$) are shown in Fig. 4. With only the group parameter information provided in Tables I and II, the EOS is used to predict the data quantitatively.

4.2. Vapor–Liquid Equilibria of Polymer Solutions

As a typical example of vapor–liquid equilibria of solutions containing a polymer in an organic solvent, the activity coefficients of a solvent in a polymer solution were predicted and compared with experiment. The activity coefficients of *m*-xylene in poly(styrene; $M_n = 247, 000$) solution were predicted by the group parameters given in Tables I and II and are compared with experiment [12] in Fig. 5. The EOS can be used to predict the data quantitatively. Similar comparisons for the predicted activity coefficients of 1,4-dioxane in poly(tetra-methylene oxide; $M_n = 650$) solution [12], for those of benzene in poly(vinylacetate; $M_n = 48, 000$) solution [12], and for those of benzene in poly(vinylmethylether; $M_n = 14, 000$) solution [12] are shown in Figs. 6–8, respectively.

Upon qualitative comparison with experiment, the GC-EOS predicts reasonably well the activity coefficients in common polymer solutions. Further error analysis of the predictions and comparisons with other GC models in the same genre [5] will be published later; we wish to demonstrate here only the basic concept of the present approach. In summary, with a single set of group parameter values, we found that the GC approach presented here can be applied to both the specific volumes of pure polymers and the phase equilibrium properties of binary polymer solutions. Since we determined the group parameters only with limited data sources, the reliability of the present approach needs to be further enhanced.

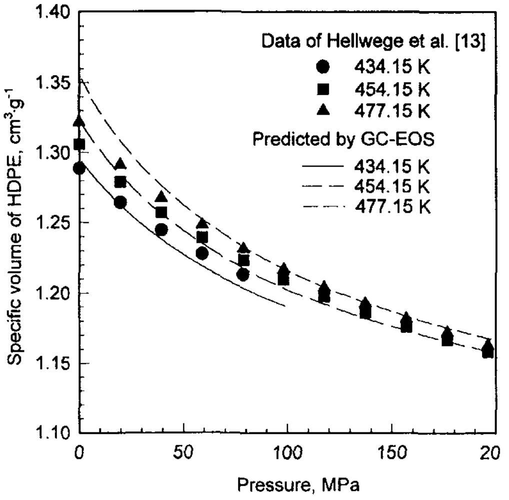

Fig. 1. Predicted specific volumes of high-density poly(ethylene).

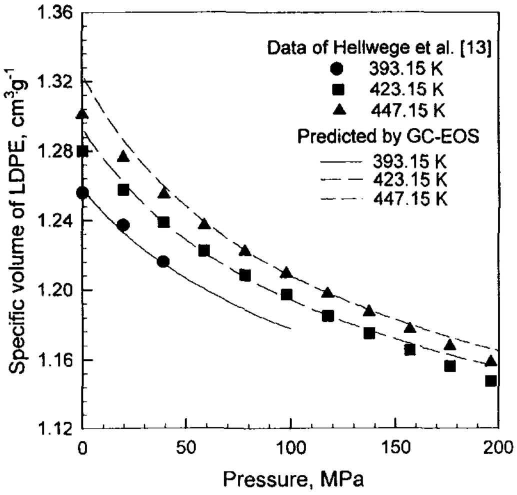

Fig. 2. Predicted specific volumes of low-density poly(ethylene).

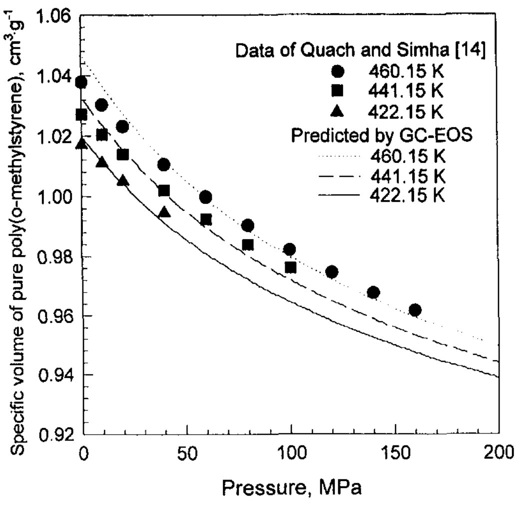

Fig. 3. Predicted specific volumes of poly(*o*-methylstyrene).

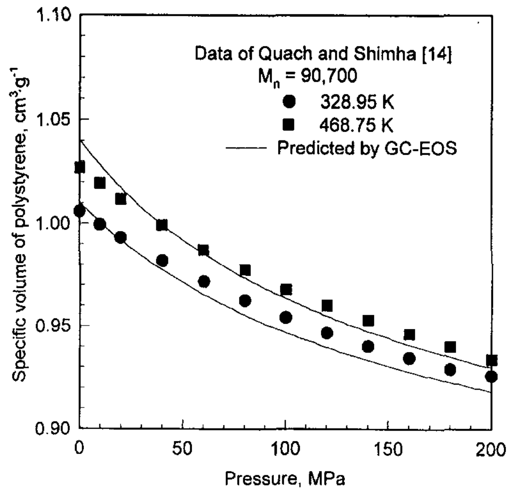

Fig. 4. Predicted specific volumes of poly(styrene).

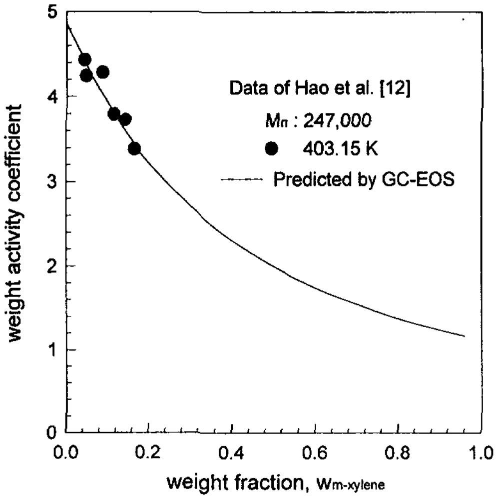

Fig. 5. Predicted activity coefficients of *m*-xylene in poly(styrene)/*m*-xylene solution.

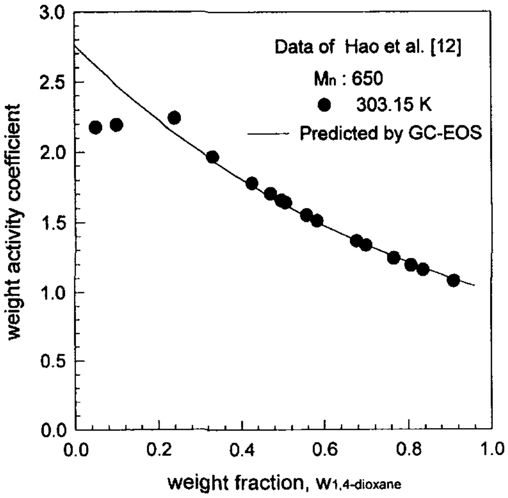

Fig. 6. Predicted activity coefficients of 1,4-dioxane in poly(tetramethylene oxide)/1,4-dioxane solution.

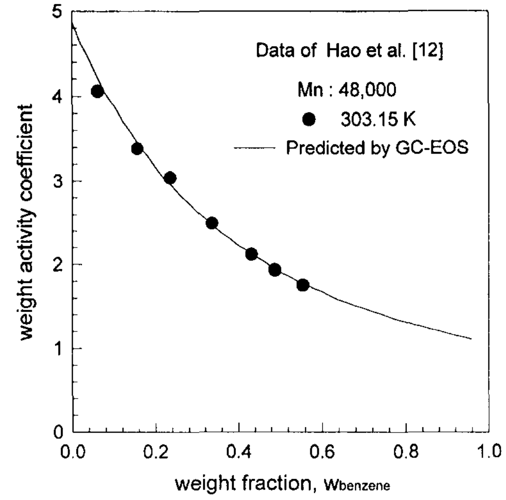

Fig. 7. Predicted activity coefficients of benzene in poly(vinylacetate)/benzene solution.

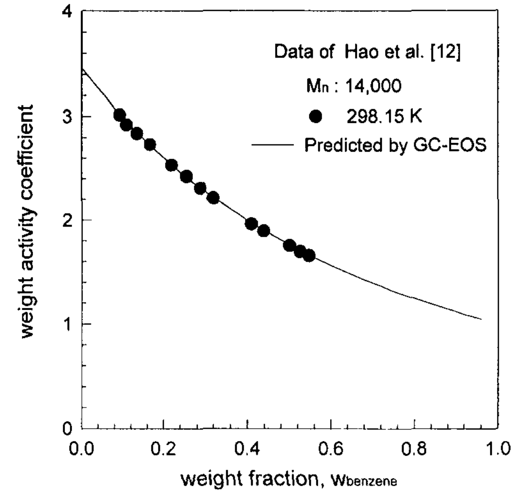

Fig. 8. Predicted activity coefficients in poly(vinylmethylether)/benzene solution.

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