Polymer Bulletin 16, 375–379 (1986)

Polymer Bulletin

Macromolecular structure of coals
X. Thermodynamic interaction parameter for solvents and coal networks

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Summary

The Flory thermodynamic interaction parameter, χ, was calculated for a range of solvents interacting with the crosslinked macromolecular structure of coals of a wide range of carbon content.

Introduction

In the first contribution of this series (1) we established that the organic phase of bituminous coals can be described as a highly crosslinked macromolecular network. In other contributions we determined the molecular weight distribution of the uncrosslinked chains found in the mesh of this macromolecular network (2), and the number average molecular weight between crosslinks, $\overline{M}_c$, of the network (3,4). Finally, using mass spectroscopy we determined the approximate size of the repeating clusters of the coal structure, a term that could be liberally called the "hypothetical repeating unit" of coal (5).

The determination of the values of $\overline{M}_c$ for coal networks requires knowledge of the Flory thermodynamic interaction parameter, χ, between solvents (swelling agents) and the coal network, and use of an appropriate swelling equation (6). Unfortunately, the only available data of χ-factors for these systems are the old, and somewhat inaccurate, results of Wynne-Jones *et al.* (7). Here, we reexamine the determination of the χ-factor for these systems and offer new more accurate values.

Analysis

The thermodynamic interaction parameter, χ, measures the compatibility of two components. This parameter is difficult to measure for solvent/polymer systems which exhibit heterogeneity and solvent specific interactions (non-randomness). Such is the case of interactions of certain solvents (especially pyridine) with the organic phase of bituminous coals (1,3). Rigorously, the Flory χ-factor is the dedimensionalized residual chemical potential, resulting from the mixing of a solvent and the macromolecular network. Thus, interactions between solvent and network become

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stronger and more favorable as the value of χ becomes more negative.

Kirov *et al.* (8) successfully used swelling equilibrium to determine the solubility parameter of coal, δ_2. They assumed that the term χ is a sum of the entropic and enthalpic mixing interactions in swelling, expressed by the parameters χ_S and χ_H, respectively.

$$\chi = \chi_S + \chi_H = \beta + \frac{V_1}{RT} A_{12} \tag{1}$$

Here A_{12} is the interchange energy density, V_1 is the molar volume of the swelling agent, and β is an entropic contribution defined in terms of the coordination number of the liquid lattice model. Then, the χ factor could be expressed as

$$\chi = \beta + \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \tag{2}$$

where δ_1 is the solubility parameter of the solvent, and δ_2 is the solubility parameter of coal, which changes with chemical character of the coal; this latter parameter is loosely associated with carbon content. Kirov *et al.* (8) used a rearrangement of this last equation to graphically calculate a value of δ_2 in a trial and error analysis of coal swelling data by seventeen solvents. The key problem with this analysis is that it does not account for solvent-specific effects such as hydrogen or π–π bonding. Neglect of such effects may prove to be crucial in determinations of χ, as recent research has shown that specific interactions in the form of electron-donor and electron-acceptor are the cause of the strong affinity and good extractability of the coal system by pyridine (1,3).

In our analysis the value of the entropic contribution, χ_S, of equation (1) was approximated as 0.3 (9). The enthalpic contribution, χ_H, is defined as

$$\chi_H = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 + 2(1 - K)\,\delta_1\delta_2 \tag{3}$$

Here, the only parameter not previously defined is the term K, a parameter intended to correct for specific interactions, such as dipole-dipole interactions or hydrogen bonds. When $K > 1$, then the interactions are favorable to dissolution, when $K < 1$, specific interactions prevent dissolution, and when $K = 1$, there are no specific interactions.

The analysis of the solubility data of Kirov *et al.* (8) was done by first accepting their values of δ_2 (see also Table 1) determined at 35 °C, and the solvent solubility parameters, δ_1, from van Krevelen (9). These data were corrected for temperature changes by defining δ_1 as

Table 1

Flory Thermodynamic Interaction Parameter for Solvents/Coal Networks at 35 ° C Derived from the Coal Solubility Parameters of Kirov *et al.* (7)

Solvent	Solvent[1] Solubility Parameter, δ_1 $(cal/cm^3)^{1/2}$	Molar[2] Volume V_1 (cm^3/mol)	Thermodynamic Interaction Parameter, χ, at 35 ° C	
			75.9%C(daf)[3] δ_2=9.8 $(cal/cm^3)^{1/2}$	88.2%(daf)[3] δ_2=9.3 $(cal/cm^7)^{1/2}$
Acetone	10.0	73.53	0.300	0.360
Cyclohexane	8.2	108.10	0.764	0.519
Ethanol	12.7	58.30	1.123	1.431
Methanol	14.5	40.50	1.801	2.137
n-Propanol	11.9	74.80	0.853	1.148
Pyridine[4]	10.6	80.56	0.386	0.528

1. Solvent solubility data from Van Krevelen (9) at 25 ° C.
2. Solvent molar volume data from Reid *et al.* (10) at 25 ° C.
3. Coal solubility data from Kirov *et al.* (7) at 35 ° C.
4. Solvent with specific effects. Values corrected as discussed in tent.

$$\delta_1 = \left[\frac{\Delta H_{vap} - RT}{V_1}\right]^{1/2} \quad (4)$$

Here ΔH_{vap} is the heat of vaporization (10) of the solvent at 25 ° C (=9,736.5 cal/mol for pyridine), which was assumed to remain constant in the range of 25-80 ° C and V_1 is the solvent molar volume at the temperature of interest. Thus, the pyridine solubility parameter, δ_1, was calculated as 10.6, 10.58, 10.42 and 10.29 $(cal/cm^3)^{1/2}$ at 25, 35, 60 and 80 ° C, respectively.

Then, the χ-factor was calculated at 35 ° C for each coal network sample for which data of the solubility parameter, δ_2, were available (see Table 1) with the assumption of negligible specific interactions (K=1 in equation (3)). For example, for the coal sample with 75.9%C (on a dry, ash-free (daf) basis), the χ-factor for the pair pyridine-coal was determined as 0.381. Similarly for coals with 82.4%C and 88.2%C the χ-factor values were determined as 0.455 and 0.518 at 35 ° C. Since pyridine is a swelling agent widely used for coal swelling studies we offer in Table 2 the results of linear regression analysis of all the values of χ-factors calculated as a function of % C (daf). The results of this analysis for a range of solvents and two coals are shown in Table 1. Based solely on this analysis, alcohols and cyclohexane are poor solvents for coals, whereas acetone, 2-butanone and pyridine are thermodynamically-good solvents (or swelling agents).

Table 2.

Pyridine-Coal Thermodynamic Interaction Parameter
Assuming no Specific Interactions of Pyridine

Temperature (°C)	Coefficients of Relation* $\chi=\alpha C-\beta$	
	α	β
35	0.012	0.466
60	0.009	0.330
80	0.007	0.226

* C=%C(daf)

Table 3.

Flory Thermodynamic Interaction Parameter for Pyridine/Coal Networks
from Equilibrium Swelling Data at Various Temperatures*

Carbon Content %C(dmmf)	Mol. Wt. Between Crosslinks at 35 °C $\bar{M}_c$	Thermodynamic Interation Parameter χ		
		35 °C	60 °C	80 °C
69.9	980	0.287	0.197	-0.331
72.2	1,030	0.321	0.267	-0.405
73.0	1,100	0.339	0.208	-0.369
77.1	1,270	0.363	0.244	-0.132
79.8	1,190	0.411	0.279	-0.130
82.5	1,260	0.419	0.232	0.123
86.0	780	0.464	-	-
88.1	1,110	0.507	-	-
91.5	780	0.549	0.367	-0.215
94.2	810	0.552	0.223	-0.121

* Results not corrected for specific effects. These results were used to determine K.

Four solvents, i.e., dimethyl formamide, methylethyl ketone, pyridine and quinidine are known to exhibit specific effects during coal swelling. For these solvents, the specific interaction parameter, K, was determined and appropriate corrections were applied to the χ-factor values determined before, using equation (3).

For example, for pyridine/coal network interactions, use was made of the data of the number average molecular weight between crosslinks, $\bar{M}_c$, of Lucht and Pep-

pas (3) which were determined at three swelling temperatures, 35, 60 and 80 ° C. Assuming that $\overline{M}_c$ remained constant for the same coal sample and that the increased coal swelling as a function of temperature was the result of specific effects due to the swelling agent, the temperature dependence of the χ-factor could be determined (see Table 3). For a specific temperature the term χ_H was calculated using equation (1) with χ_S=0.3. Finally, A_{12} was determined as 1.186 from these values for pyridine. Then, using equations (1) and (3) the specific effects interaction parameter K was calculated as 1.001, 1.005 and 1.008 for 35, 60 and 80 ° C, respectively.

The χ-factors for various coals interacting with the solvents exhibiting specific effects are shown in Table 4 for 35 ° C.

Conclusions

Using a detailed thermodynamic analysis of solvent/coal network interactions, including specific effects where necessary, we were able to calculate new values of the χ-factor for pyridine and other solvents from 35 to 80 ° C.

Acknowledgments

This work was supported by the Department of Energy of the USA (grant No. DE-FG22-78ET 13379).

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Accepted September 3, 1986 C