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Computational study of the process of polymer swelling in organic solvents†

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ABSTRACT: No satisfactory quantitative relationships exist between polymer swelling parameters and some distinct physical-chemical parameters of organic solvents producing this swelling. Such relationships can only be obtained by means of linear multiparameter equations, which take into account the energy needed for cavity formation in solvents and also solvation effects. The advantages of such an approach are supported by examples of the generalization of experimental data for the swelling of many polymers and coals. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: polymers; coal; swelling; organic solvents; correlation analysis

INTRODUCTION

The swelling of synthetic polymers dispersed in organic solvents is of theoretical and practical significance. It is important for determining their stability in various media when used as construction materials and also for their possible regeneration and waste utilization. In addition to synthetic polymers, the swelling of natural polymers and coals in organic solvents is of equal importance. However, the hitherto performed theoretical treatments have not afforded satisfactory correlations between the experimental swelling parameters (usually the increase in weight or the volume extension of the swelling polymers) and physical-chemical characteristics of the solvents used. The correlations obtained have at best only qualitative or semi-quantitative character and, as a rule, require the introduction of numerous empirical correcting coefficients. We refer to the swelling process treatment,[1–4] based on Hildebrand's regular solution theory.[5] According to this theory, the inter-solubility of the system components is determined by the cohesion energy of the phases involved, characterized by Hildebrand's solubility parameter, δ, defined as

$$\delta = [(\Delta H_{\mathrm{vap}} - RT)/V_{\mathrm{M}}]^{0.5} \qquad (1)$$

where ΔH_{vap} is the solvent's enthalpy of vaporisation and V_{M} its molar volume.

A maximum of mutual solubility is observed when the differences in the solubility parameters of both phases are minimal or equal to zero. Correspondingly, the interrelation between the degree of polymer swelling or polymer solubility and the δ values of organic solvents is represented by a bell-like curve with a maximum for those solvents for which $\delta_{\mathrm{solvent}} = \delta_{\mathrm{polymer}}$. Typical examples are given by the swelling data determined for polyethylene and poly(styrene-*co*-divinylbenzene),[6,7] and also for 'Big Brown' lignite[8] and vulcanized natural rubber[4] (Table 1). The correlations between the swelling parameters W and the solubility parameter δ are unsatisfactory (Fig. 1). In the case of vulcanized rubber, the curve obtained splits in general into two branches—an upper branch, which includes mainly the data for ketones and esters, and a lower branch, for aromatic hydrocarbons and halohydrocarbons. However, in reality, for most correlations severe deviations are observed, and some data do not correspond even qualitatively to such branches. Owing to such correlations and also the uconventional shape of the curves, the divergent curves obtained do not allow one to calculate quantitatively the swelling parameters for other solvents. Similar peculiarities are also observed for the case of coal extraction.[9]

As a result of these uncertainties, especially in the chemistry of coal, many authors, who used only the physical model of the swelling process, declimed to carry out further investigations and, moreover, suggestions appeared that swelling is mainly caused by chemical interactions.[10] However, a comparison of the experimental swelling or extraction parameters with solvent parameters describing the specific solvation ability of solvents, such as the donor (DN) or acceptor numbers (AN) introduced

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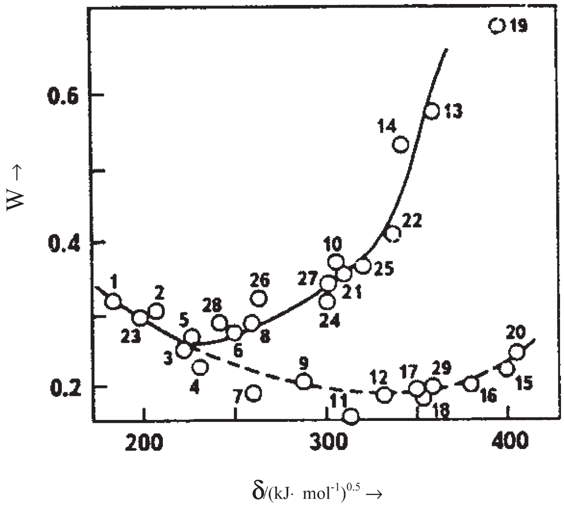

Figure 1. Interrelation between the swelling degree, *W*, of vulcanized natural rubber ('smoked ship') (volume part of polymer in the swollen sample) and the solvent's solubility parameter δ. The solvent numbering corresponds to that in Table 1

by Gutmann,[11] Reichardt's[12] electrophilicity parameters E_T, or Palm's basicity B parameters also leads only to qualitative correlations with numerous deviations. Examples of the above are the correlation of the outputs of extracts from a bituminous coal with the solvent donor numbers[10] and the solvation of peptide resins.[13]

In later investigations,[14,15] it was found that linear dependences between the degree of swelling of various polymers and different solvent parameters exist only for separate groups of solvents, e.g. for hydrocarbons, alcohols, ketones, esters, etc.

These discrepancies found in the correlation are caused by the fact that one-parameter equations applied to swelling or extraction processes take into account only the factors dependent on physical solute–solvent interactions and do not consider the possible influence of other more specific solute–solvent interactions. A similar situation existed until recently with the correlation analysis of the solvent influence on rates of chemical processes or on spectral absorptions. A solution of this problem was found by using the linear free energy principle (LFER), which states that the change in a solute's free Gibbs energy, ΔG, for the passage from the gas phase into solution is determined by the summation of all possible, mutually independent energetic effects g_i, stemming from the various non-specific and specific solvation processes according to the equation

$$\Delta G = \Sigma gi \qquad (2)$$

Such an approach was widely used first by Koppel *et al.*[16] and then by Kamlet *et al.*[17] One should point out that both schools consider in principle the same combination of solvent effects, but, described by different numerical scales.

We have applied this approach to the correlation analysis of solution and extraction processes of polymers. As the passage of solute molecules from one phase to the other requires an expenditure of energy for their penetration into the other phase, it was therefore necessary to take into account this kind of interaction. According to the views of Pierotti on the solubility of gases[18] and of Mayer on the solubility of solids or the ion distribution between two phases,[19] the total energetic outcome of such processes, $\Delta H_{\text{solution}}$, can be estimated as the algebraic sum of the energy expenditure necessary for cavity formation in order to accommodate the foreign molecules in the liquid and of the energy gain as result of their subsequent solvation, as described by the equation

$$\Delta H_{\text{solution}} = \Delta H_{\text{cavity}} + \Delta H_{\text{solvation}} \qquad (3)$$

The first term is proportional to the cohesion energy of the solvent, which is determined by the square of Hildebrand's solubility parameter, δ^2, and the second solvation term can be determined on the basis of Koppel *et al.*'s or Kamlet *et al.*'s approaches. The verification of this supposition permits one to generalize satisfactorily the influence of the solvent properties on the solubility of gases or solids[20,21] and also on the distribution of organic or inorganic compounds between water (a standard phase) and an organic phase.[22]

This approach was used by us both for the correlation analysis of the swelling data for various polymers, including the swelling data for coals, determined in organic solvents of different chemical character[23] and for data on their extraction.[24] For these calculations we used the following equation:

$$\log K = a_0 + \frac{a_1(n^2-1)}{n^2+2} + \frac{a_2(\varepsilon_r-1)}{2\varepsilon_r+1} + a_3\delta^2 + a_4B + a_5E_T \qquad (4)$$

where K is the conventional equilibrium constant of the thermodynamic equilibrium process:

$$\text{polymer} + \text{solvent} \overset{K}{\rightleftharpoons} \text{swollen polymer}$$

equal to the ratio of weight or volume of the swollen polymer to that of the initial polymer and n, δ_r, B, E_T and δ^2 are the refractive index, relative electric permittivity, Palm's basicity, Reichardt's electrophilicity and Hildebrand's solubility parameters, respectively, of the organic solvents used. The regression coefficients a_i are calculated by means of the least-squares method. According to IUPAC recommendations,[25] the validity of these calculations was controlled by the Fisher criterion (at $\alpha = 0.95$) and the multiple correlation coefficient R ($R > 0.95$).

RESULTS AND DISCUSSION

The multiparameter approach described was useful for the correlation analysis of many series of swelling data for polymers and solid coals, dispersed in various organic solvents, taken from our own experiments and from the literature. As an example, we present here the results of the treatment of swelling data for ‘smoked ship’ rubber, expressed by its swelling equilibrium constant $K = W/(1 - W)$, where W is the weight [% (mg g^{-1})] of absorbed solvent (Table 1).[4] As mentioned previously, these swelling data exhibit no correlation with singular solvent characteristics, but for most of the solvents they can be satisfactorily correlated by means of a five-parameter equation with $R = 0.958$. From the initial data available for 29 solvents, seven strongly deviating ones were excluded ($n = 22$) and satisfactory results were obtained with the following simplified four-parameter equation:

$$\log K = 2.262 - (12.9 \pm 1.8) f(n^2) - (3.57 \pm 0.69) f(\varepsilon_r) + (4.00 \pm 0.56) \times 10^{-3} B + (4.32 \pm 1.00) \times 10^{-3} \delta^2 \quad (5)$$

$$(R = 0.952; s = \pm 0.115)$$

More detailed results are presented in elsewhere.[26]

Analogously, previously[27] we tried to correlate the data taken from Ref. 4, dealing with the swelling of butadiene-styrene, butadiene-acrylonitrile and other synthetic rubbers, measured in 15–17 solvents. In all cases, after exclusion of strongly deviating data for some solvents, we obtained correlation equations connecting the equilibrium constant of the swelling process, K, with the physical-chemical properties of solvents with satisfactory precision. Thus, for butadiene-styrene rubber with a butadiene content of 96% by weight, the correlation equation obtained indicates that the value of K increases with increasing solvation characteristics. In contrarsty, the value of K decreases with increasing cohesion (self-association) process, since some expense of energy to break the structure of the liquid phase is necessary. Similar regularities were found for Buna rubber samples with a greater content of styrene, namely 12.5 and 28.5% by weight. The solvent’s ability for non-specific solvation also has a decisive influence on the extent of the swelling process for these rubbers. The solvents polarizability and the specific solute–solvent interactions are of little importance. Therefore, one can accept a uniform mechanism of the swelling process in these cases.

Table 1. Experimental (according to Ref. 4) and calculated values [according to Eqn (5)] of volume part of polymer in the swollen sample W, and the logarithms of the equilibrium constants of the swelling process, $\log K = \log [W/(1 - W)]$, for ‘smoked ship’ vulcanized rubber

No.	Solvent	W_{exp}	Log K_{exp}	Log K_{calc}	$\Delta\log K$	W_{calc}
1	Isopentane	0.3390	−0.2900	−0.3620	−0.0729	0.3024
2	*n*-Pentane	0.3165	−0.3344	−0.2952	0.0392	0.3363
3	*n*-Hexane	0.2506	−0.4757	−0.3633	0.1124	0.3023
4	*n*-Heptane	0.2326	−0.5184	−0.4409	0.0775	0.2660
5	*n*-Octane	0.2710	−0.4298	−0.4638	−0.0341	0.2558
6	*n*-Decane	0.2725	−0.4265	−0.5516	−0.1252	0.2192
7	Methylcyclohexane	0.1901	−0.6295	−0.6077	0.0218	0.1979
8	*n*–Dodecane	0.2874	−0.3944	−0.5988	−0.2044	0.2012
9	Cyclohexane	0.1866	−0.6394	−0.5169	0.1255	0.2332
10	1,1,1-Trichloroethane	0.1799	−0.6588	−0.7142	−0.0554	0.1619
11	Tetrachloromethane	0.1508	−0.7506	−0.7309	0.0197	0.1567
12	Toluene	0.1837	−0.6477	−0.6646	−0.0169	0.1779
13	Ethyl methyl ketone	0.5799	0.1391	0.1270	−0.0122	0.5726
14	Ethyl acetate	0.5282	0.0490	0.2260	0.1770	0.6272
15	1,1-Dichloroethane	0.2155	−0.5612	−0.4581	0.1031	0.2583
16	Bromoethane	0.1984	−0.6064	−0.4848	0.1216	0.2467
17	Benzene	0.1931	−0.6210	−0.5983	0.0227	0.2014
18	Trichloromethane	0.1558	−0.7339	−0.7906	−0.0567	0.1394
19	Acetone	0.8307	0.6908	0.4636	−0.2272	0.7441
20	Dichloromethane	0.2347	−0.5133	−0.5941	−0.0807	0.2030
21	Methyl pentyl ketone	0.3559	−0.2576	−0.2033	0.0543	0.3050
22	Diethyl ketone	0.4098	−0.1584	−0.1448	0.0137	0.4174
23	Isooctane[a]	0.3003	−0.3674	−0.6123	−0.2450	0.1963
24	*n*-Butyl acetate[a]	0.3236	−0.3202	−0.1174	0.2028	0.4329
25	Ethyl propionate	0.3676	−0.2356	0.0573	0.2929	0.5329
26	*n*-Hexadecane[a]	0.3226	−0.3222	−0.6496	−0.3275	0.1830
27	1,2-Dichloroethane[a]	0.3401	−0.2879	−0.7599	−0.4720	0.1481
28	Diethyl ether[a]	0.2899	−0.3891	0.4433	0.8327	0.7351
29	Tetrahydrofuran[a]	0.1923	−0.6233	0.4249	1.0481	0.7268

[a] These solvents were not used for the calculations using Eqn (5).

As expected, the swelling behaviour of butadiene-acrylonitrile rubbers, containing a strongly dipolar nitrile group, is clearly opposite that of butadiene-styrene rubbers.

However, in spite of the generally acceptable results, the methods of calculation offered by Eqn (4) require exclusion of some experimental data from the calculations in order to obtain satisfactory results for a sufficiently large number of solvents. Taking into account that a larger size of a solvent molecule hinders its penetration into the polymer network, the correlation analysis can be improved by including a sixth term in Eqn (4) that takes into account the solvent's molar volume, V_M, according to Ref. 15:

$$\log S = a_0 + \frac{a_1(n^2-1)}{n^2+2} + \frac{a_2(\varepsilon_r - 1)}{2\varepsilon_r + 1} + a_3 B + a_4 E_T + a_5 \delta^2 + a_6 V_M \qquad (6)$$

where S is the moles of solvent absorbed by the polymer sample.

The quantity of solvent absorbed by standard quantity of a polymer to a first approximation is proportional to the constant of an equilibrium process, and in accordance with the principles of chemical thermodynamics $\log K$ of the equilibrium is a linear dependence on the free energy change. That is why in Eqns (4)–(6) and here after we do not introduce in to the calculations the actual quantity absorbed but its logrithmic value.

It was found that Eqn (6) describes the experimental data sets for the degrees of swelling of different polymers much better than Eqn (5).

The V_M term is of great significance and permits one to exclude some less important terms of Eqn (6). As expected, in all correlation equations it was found that V_M is negative, that is, increasing the solvent's molar volume reduces the extent of its penetration into the polymer. The swelling degree S_M of a polymer is usually given as the moles of solvent absorbed by a unit mass or unit volume of the polymer. The results obtained by using these units of S_M are noticeably better than those obtained by using the values of S given in mass or volume percent, or as equilibrium constants, $K = S/(1-S)$, used by us in our earlier work.

As an example, we present here the results of the correlation analysis of the data given in Ref. 15 for the swelling of synthetic poly-*cis*-isoprene.[28]

Table 2 gives the S_M data from Ref. 15 for the swelling of natural rubber membranes at 25, 44, and 60 °C, measured in 27 solvents.

Attempts at correlating these data obtained at 25 °C for all 27 solvents by means of Eqn (6) led to an equation with an unsatisfactorily low multiple correlation

Table 2. Amounts of solvents, S_M (mol), absorbed by poly-*cis*-isoprene at 25 °C (according to Ref. 15), and the corresponding values of $\log S_M$, based on experimental and calculated values [according to Eqn (8)]

		S_M			Log S_M(25 °C)	
No.	Solvent	25 °C	44 °C	60 °C	Exp.	Calc.
1	*n*-Hexane	0.807	0.797	0.784	−0.093	−0.109
2	*n*-Heptane	0.718	0.718	0.708	−0.144	−0.140
3	*n*-Octane	0.648	0.661	0.667	−0.188	−0.201
4	Isooctane	0.562	0.555	0.548	−0.250	−0.179
5	*n*-Nonane	0.607	0.607	0.616	−0.216	−0.218
6	*n*-Decane	0.526	0.532	0.553	−0.279	−0.267
7	*n*-Dodecane	0.408	0.422	0.452	−0.389	−0.363
8	*n*-Tetradecane	0.339	0.348	0.361	−0.470	−0.446
9	*n*-Hexadecane	0.282	0.295	0.336	−0.550	−0.574
10	Cyclohexane	1.495	1.517	1.534	0.175	−0.082
11	Tetralin	1.306	1.330	1.348	0.115	0.198
12	Benzene	1.890	1.880	1.880	0.276	0.247
13	Toluene	1.670	1.650	1.670	0.223	0.173
14	*p*-Xylene	1.500	1.480	1.450	0.176	0.100
15	1,3,5-Trimethylbenzene	1.170	1.190	1.190	0.068	0.042
16	Chlorobenzene	1.870	1.830	1.890	0.217	0.262
17	Fluorobenzene	1.650	1.670	1.610	0.272	0.177
18	Bromobenzene	1.780	1.790	1.820	0.250	0.313
19	Nitrobenzene[a]	0.520	0.640	0.740	−0.284	0.285
20	Aniline[a]	0.080	0.110	0.150	−1.897	0.139
21	Cyclohexanone	1.094	1.182	1.325	−0.009	−0.068
22	Methyl acetate[a]	0.224	0.263	0.292	−0.650	−0.101
23	Ethyl acetate	0.462	0.538	0.586	−0.335	−0.138
24	*n*-Propyl acetate	0.612	0.678	0.719	−0.213	−0.193
25	*n*-Butyl acetate	0.666	0.730	0.862	−0.176	−0.212
26	Isoamyl acetate	0.610	0.644	0.778	−0.214	−0.285

[a] Excluded from calculations.

coefficient $R = 0.881$. However, after excluding the data for only three deviating solvents (aniline, nitrobenzene and methyl acetate; $n = 24$), we obtained Eqs (7) and (8) with satisfactory correlation coefficients $R = 0.966$ and 0.964, respectively.

$$\begin{aligned}\log S_{\mathrm{M}} = {} & -0.501 + (4.00 \pm 1.29)f(n^2) \\ & + (0.42 \pm 0.90)f(\varepsilon_{\mathrm{r}}) - (0.59 \pm 0.04) \times 10^{-3}B \\ & - (1.41 \pm 25.6)E_{\mathrm{T}} + (0.04 \pm 0.87) \times 10^{-3}\delta^2 \\ & - (3.72 \pm 0.36) \times 10^{-3}V_{\mathrm{M}} \qquad (7)\end{aligned}$$

$$\begin{aligned}\log S_{\mathrm{M}} = {} & -0.503 + (3.91 \pm 0.51)f(n^2) \\ & - (0.88 \pm 0.20) \times 10^{-3}B \\ & - (3.64 \pm 0.31) \times 10^{-3}V_{\mathrm{M}} \qquad (8)\end{aligned}$$

The $\log S_{\mathrm{M}}$ values calculated by Eqn (8) are given in Table 2 together with their deviations from the experimental values.

The swelling data for poly-*cis*-isoprene obtained at 44 and 60 °C can be correlated in a similar way; the signs and significance of separate terms in the corresponding equations are identical for all three temperatures, and the regression coefficients are close to each other.

Excellent results are obtained in the correlation analysis of the data for an ethylene–propylene–butadiene copolymer, the swelling of which was studied in 27 solvents.[15] After the exclusion the value of only one solvent (nitrobenzene; $n = 26$), the R value becomes 0.955. It also turned out that the terms δ^2 and B are unimportant and can be omitted from the correlation equation.[29] Satisfactory results were also obtained in the correlation analysis of the data given in Ref. 6 for the swelling of polyethylene (average molecular mass 9400), studied in 30 solvents.

It was found that Eqn (6) is also adequate for the correlation analysis of the data on the swelling of a series of other polymers, (non-polar and polar), while taking into account that the importance of some of the equation's terms (solvation factors) depend on the polymer structure and especially those containing substituent groups. As an example, we present here the results of the correlation analysis of the data given in Refs 15 and 30–32 on the swelling of polyurethane rubber [a copolymer of poly(propylene oxide) and toluylene diisocyanate], determined in 38 solvents (Table 3).

The correlation analysis of the data in Table 3 by Eqn (6) leads to a correlation equation with an unsatisfactorily low multiple correlation coefficient $R = 0.943$, although the equation obtained is sufficiently precise according to Fisher's criterion for the corresponding degrees of freedom at a reliable degree of $\alpha = 0.95$. Exclusion of only two deviating solvents from the calculations (1,1,2,2-tetrachloroethane and cyclohexanone) leads to Eqn (9) with an acceptable value of $R = 0.965$:

$$\begin{aligned}\log S = {} & -0.002 + (6.93 \pm 0.93)f(n^2) \\ & + (1.30 \pm 0.69)f(\varepsilon_{\mathrm{r}}) + (1.00 \pm 0.55) \times 10^{-3}B \\ & - (3.13 \pm 17.1) \times 10^{-3}E_{\mathrm{T}} - (1.04 \pm 0.57) \times 10^{-3}\delta^2 \\ & - (10.8 \pm 1.09) \times 10^{-3}V_{\mathrm{M}} \qquad (9)\end{aligned}$$

$$(N = 36, R = 0.965, s = 0.128)$$

Because of the insignificance of the E_{T} parameter ($R = 0.965$) and the small significance of B ($R = 0.961$), both terms can be omitted to give

$$\begin{aligned}\log S = {} & -0.14 + (6.39 \pm 0.66)f(n^2) + (1.97 \pm 0.35)f(\varepsilon_{\mathrm{r}}) \\ & + (1.06 \pm 0.31) \times 10^{-3}\delta^2 \\ & - (10.4 \pm 1.08) \times 10^{-3}V_{\mathrm{M}} \qquad (10)\end{aligned}$$

$$(N = 36, R = 0.961, s = 0.131)$$

The multiparameter correlation between the experimental and calculated $\log S$ values for polyurethane according to Eqn (9) is presented in Fig. 2.

An analysis of the signs of the terms of in Eqn (9) shows that an increase in the solvent's molecular size (molar volume V_{M}) lowers its capacity for penetration into the polymer network, as shown by the negative sign of V_{M}. A similar negative sign is obtained for the δ^2 terms describing the association of the solvent (since the necessary expenses of energy are increased owing to the tearing off of some molecules from the liquid structure), and for the electrophilic solvation term E_{T}. This is possible owing to the large E_{T} values, which are typical of solvents capable of self-association, such as alcohols.

The terms $f(n^2)$ and $f(\varepsilon_{\mathrm{r}})$ in Eqn (9) have positive signs, suggesting the presence of non-specific solvation of polymer chains by the absorbed solvent.

The value of $\log S$ diminishes with increase in the solvent's molar volume. The parameter V_{M} alone cannot characterize the relations between the degree of swelling of polyurethane in solvents. Sometimes linear correlations can be observed only for separate groups of solvents such as *n*-alkanes and primary alcohols, in accordance with Ref. 15.

The high significance of the $f(n^2)$ term in Eqn (9) is in agreement with the presence of many benzene rings in the polyurethane polymer.

Table 3 contains the $\log S$ values for polyurethane swelling at 25% calculated by Eqn (10) and their deviations from the experimental values given as $\Delta\log S$.

The data on the swelling of polyurethane measured at 44 and 60 °C can also be adequately described by Eqn (6).

It is shown that multiparameter equations such as Eqn (6) are also suitable for correlation analysis of the

Table 3. Logarithms of the degree of swelling, log *S*, of polyurethane, based on experimental values of *S*, determined at 25 °C (see Refs. 15 and 30–32), and calculated values [according to Eqn (10)]

No.	Solvent	Q (mmol g^{-1})	Log S_{exp}	Log S_{calc}	Δlog S	V_M (cm^3 mol^{-1})
1	*n*-Hexane	0.950	−0.0223	0.0870	−0.109	131.61
2	*n*-Heptane	0.687	−0.1630	−0.0305	−0.133	147.46
3	*n*-Octane	0.542	−0.2660	−0.1576	−0.108	162.60
4	Isooctane	0.510	−0.2924	−0.1626	−0.130	165.10
5	*n*-Nonane	0.473	−0.3251	−0.2904	−0.0348	178.64
6	*n*-Decane	0.354	−0.4510	−0.4434	−0.0076	194.89
7	Cyclohexane	2.080	0.3181	0.4758	−0.158	108.09
8	Benzene	9.160	0.9619	0.8864	0.0755	89.41
9	Toluene	6.780	0.8312	0.7406	0.0906	106.85
10	*p*-Xylene	5.430	0.7348	0.5645	0.170	123.30
11	Mesitylene	3.530	0.5478	0.3992	0.149	139.11
12	Tetralin	4.590	0.6618	0.5828	0.0790	136.27
13	Tetrachloromethane	6.880	0.8376	0.7425	0.0951	96.50
14	1,2-Dichloroethane	12.86	1.109	1.172	−0.0633	78.74
15	1,1,2,2-Tetrachloroethane	31.06	1.492	—	—	104.74
16	Trichloroethene	12.60	1.100	0.9642	0.136	89.74
17	Tetrachloroethene	5.020	0.7007	0.7662	−0.0655	102.42
18	Chlorobenzene	10.15	1.006	1.101	−0.0950	101.79
19	Tribromomethane	22.09	1.344	1.315	0.0296	87.42
20	1,2-Dibromoethane	9.870	0.9943	1.196	−0.202	86.21
21	Bromobenzene	9.950	0.9978	1.121	−0.123	105.03
22	Methanol	7.780	0.8910	0.7400	0.151	40.41
23	Ethanol	7.250	0.8603	0.8760	−0.0156	58.37
24	*n*-Propanol	6.320	0.8007	0.8687	−0.0680	74.70
25	2-Propanol	4.180	0.6212	0.8479	−0.227	76.54
26	*n*-Butanol	6.380	0.8048	0.7809	0.0239	91.53
27	Isobutanol	5.250	0.7202	0.7688	−0.0487	92.34
28	2-Butanol	4.490	0.6522	0.7797	−0.127	91.93
29	Isopentanol	4.700	0.6721	0.6609	0.0112	108.56
30	Anisole	8.030	0.9047	0.9409	−0.0362	109.31
31	Cyclohexanone	37.07	1.569	—	—	103.56
32	Methyl acetate	7.790	0.8915	0.8178	0.0738	80.14
33	Ethyl acetate	5.870	0.7686	0.6935	0.0751	97.78
34	*n*-Propyl acetate	5.370	0.7300	0.5735	0.156	115.15
35	*n*-Butyl acetate	4.280	0.6314	0.4170	0.214	131.63
36	Isoamyl acetate	3.320	0.5211	0.2449	0.276	149.32
37	Methyl benzoate	8.190	0.9133	0.8478	0.0655	125.05
38	Diethyl malonate	2.200	0.3424	0.4635	−0.121	151.78

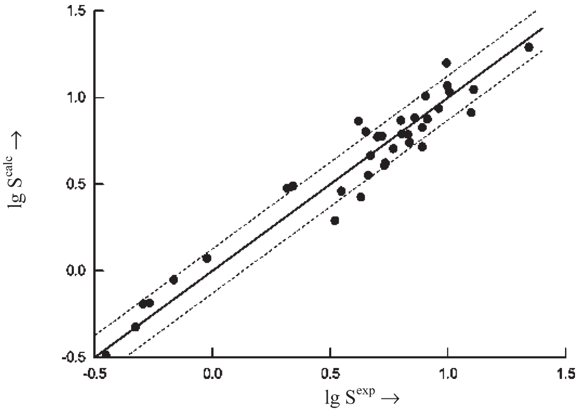

Figure 2. Correlation between the logarithms of the experimental and calculated [according to Eqn (9)] values of *S* for samples of polyurethane

swelling data for polyurethane rubbers; in addition, the same terms of the multiparameter equation are significant as found for polymers which do not contain dipolar groups, namely, the molar volume of the solvents and their capacity for non-specific solvation.

Linear multiparameter equations not only permit the correlation analysis of experimental swelling data for polymers but also help to predict their degrees of swelling in other yet unexplored solvents on the basis of their physical and chemical properties, and to draw conclusions about the mechanism of the swelling processes. As an example, we present here the results of a correlation analysis of the swelling data of Illinois coal No. 6, measured in nine solvents (Table 4) and taken from Ref. 33. There is no relation at all (Fig. 3) between the quantity of absorbed liquid *W* and dose δ^2 and between log *S* and V_M or *B*. An approximate decrease or increase with increase in the determined parameter is observed. At the same time, the application of a six-paramer equation

Table 4. Degrees of Swelling, S_M, of Illinois coal, taken from experiment (Ref. 33) and calculated from the three-parameter Eqn (11) ($R=0.991$; $s=0.023$)

		Experimental			Calculation		
No.	Solvent	W	$S_M \times 10^{-3}$	$\log S_M$	$\log S_M$	$\Delta\log S_M$	Δ (%)
1	Pyridine	1.87	11.00	−1.959	−1.958	−0.001	0.1
2	1,4-Dioxane	1.64	7.264	−2.139	−2.143	0.005	0.2
3	Dichloromethane	1.60	7.064	−2.151	−2.179	0.028	1.3
4	Chlorobenzene	1.48	4.264	−2.370	−2.364	−0.006	0.3
5	2-Propanol	1.45	7.489	−2.126	−2.136	0.011	0.5
6	Toluene	1.41	4.450	−2.352	−2.364	0.013	0.5
7	Ethanol	1.40	8.682	−2.061	−2.069	0.008	0.4
8	Benzene	1.38	4.864	−2.313	−2.283	−0.030	1.3
9	Acetonitrile	1.34	8.283	−2.082	−2.056	−0.026	1.2
10	Cyclohexane[a]	1.11	1.307	−2.884	—	—	—

[a] Not included in the calculation.

permits excellent correlation analysis of the data ($R=0.996$). A satisfactory result is obtained in the case when only two parameters are used:[34]

$$\log S_M = -1.96 + (0.665 \pm 0.074) \times 10^{-3} B - (4.12 \pm 0.58) \times 10^{-3} V_M \tag{11}$$

$$(N = 9, R = 0.984, s = 0.030)$$

According to Eqn (11), high V_M values (negative sign of V_M) counteract the coal swelling, whereas the second significant term, the solvent's basicity B (positive sign), favors this process, obviously because of specific solvation of the acid in centers in the coal macromolecules. Their presence stems from the considerable content of oxygen in Illinois coal. For basicity B a correlation with S_M is observed, but worse than in the case of the molar volume V_M. A comparison of these dependences confirms the conclusion about opposite contributions of these factors in the swelling process; however, their linear combination is satisfactorily proportional to the values of $\log S_M$. The third significant factor, the cohesion energy of the solvents, is proportional to the expense of energy needed to tear off an absorbed molecule from the structure of the liquid phase. This also decreases the swelling. However, its influence is insignificant, which is proved by an insignificant K value decreasing after exclusion of this factor ($R=0.991$ and 0.984, respectively). The non-specific and electrophilic solvations do not really affect the values of $\log S$.

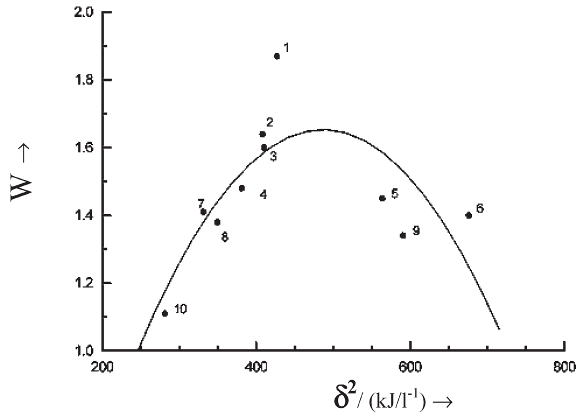

Figure 3. Interrelation between the volume degree, W, of Illinois coal No. 6 (Ref. 33) and the square of Hildebrand's solubility parameter, δ^2. The solvent numbering corresponds to that in Table 1

Finally, linear multiparameter equations are useful not only for correlation analysis of the data for polymer swelling dispersed in organic solvents, but also for the diffusion rates of solvents in polymers, which have been studied for butadiene-styrene and isoprene-styrene block copolymers.[28]

CONCLUSION

The application of multiparameter equations, containing various orthogonal terms that describe separately the different non-specific and specific solute–solvent interactions, for the correlation analysis of the swelling data for synthetic and natural polymers dispersed in organic solvents is much more successful than the one-parameter approaches proposed in earlier attempts to complete swelling data with solvent parameters.

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