A Flory–Huggins model based on the Hansen solubility parameters

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Abstract

The Hansen solubility parameters are typically used, especially in the paint and coatings industry, for selecting suitable solvents for polymer binders. In such applications, the radius of solubility needs to be determined by experiments. Moreover, other calculations, e.g. related to drying of paints, require thermodynamic description over extended concentration ranges. On the other hand, the well-known Flory–Huggins model captures satisfactorily several of the characteristics of polymer solutions, but the interaction parameter of the model usually also has to be determined by experiments.

In this work, we present a methodology, based on which the Hansen solubility parameters can be incorporated in the Flory–Huggins model. The resulting model is predictive and yields good predictions of solvent activity coefficients at infinite dilution in several acrylate and acetate polymers. The results are as accurate as other predictive polymer models based on the group-contribution (GC) principle, but in contrast to these models, knowledge of molecular structures is not required in the Hansen/Flory–Huggins model. The new model makes thus use of the extensive literature of Hansen solubility parameters, which are tabulated for very many solvents, pigments and polymers.
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1. Introduction

Hansen solubility parameters are widely used by the paint and coatings industry for selecting suitable solvents for polymeric resins. Hansen parameters can be linked to the regular solution theory, as shown below.

In the regular solution theory of Hildebrand, the solubility parameter is defined as:

$$\delta_i^2 = \frac{\Delta_{vap} u_i}{v_i} \tag{1}$$

where $\Delta_{vap} u_i$ is the molar energy of vaporization. According to the Hansen solubility parameter theory, the energy of vaporization can be divided into contributions from non-polar (dispersion) forces (d), polar forces (p) and hydrogen-bonding (hb) effects, i.e. the Hildebrand solubility parameter can be expressed in terms of the three solubility parameters related to each contribution, the Hansen solubility parameters:

$$\delta_i^2 = \delta_{i,d}^2 + \delta_{i,p}^2 + \delta_{i,hb}^2 \tag{2}$$

For regular solutions it has been found empirically that miscibility between a polymer and a solvent is achieved when the difference between the solubility parameter is below 1–$1.8\,(cal/cm^3)^{0.5}$ [1]. Similarly, for solutions where polar forces and hydrogen-bonding effects play a role, it was found by Hansen that miscibility requires that a weighted sum of squared differences for the three solubility parameter increments (d, p and hb) is less than a certain value characteristic for each polymer. The ratio of these differences was found always to be close to (4:1:1), i.e. good solvents for a polymer should be located within a sphere of radius R_2 in a $(2\delta_d, \delta_p, \delta_{hb})$ coordinate system. Thus, complete miscibility is obtained when the solubility distance D_{12} is lower than the solubility radius R_2:

$$D_{12} = \sqrt{4(\delta_{1,d} - \delta_{2,d})^2 + (\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,hb} - \delta_{2,hb})^2} < R_2 \tag{3}$$

where subscripts 1 and 2 denote the solvent and the polymer, respectively.

In contrast to the above two rules of thumb, which give only a qualitative measure of miscibility (soluble/non-soluble), the Flory–Huggins model can be used quantitatively for estimation of phase equilibria. The Flory–Huggins model in terms of activity coefficients is, for a binary system, written as:

$$\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + 1 - \frac{\phi_1}{x_1} + \chi_{12} \phi_2^2 \tag{4}$$

where ϕ and x are the volume fractions and mole fractions, respectively, and χ is the composition-independent Flory–Huggins interaction parameter. Usually, the Flory–Huggins model is based on volume fractions, as in Eq. (4). However, in some cases segment (van der Waals volume) fractions are used instead of volume fractions. In this work, we have also investigated a version based on free-volume fractions, following the reasoning behind the EFV model that free-volume fractions give a better representation of entropic effects both caused by differences in free-volume percentages (compressibilities) as well as in sizes and shapes [2].

In polymer thermodynamics, activity coefficients based on weight fractions are much wider used than mole fraction based ones. The weight fraction based activity coefficient is denoted by Ω, and relates in the following way to the activity:

$$a_i = \gamma_i x_i = \Omega_i w_i \Rightarrow \Omega_i = \gamma_i \frac{x_i}{w_i} \tag{5}$$

For highly asymmetric systems, Ω_i is much better scaled than γ_i because of very low mole fractions of high-molecular-weight compounds dissolved in solvents.

According to the regular solution theory, the relationship between the Flory–Huggins interaction parameter and the solubility parameters is:

$$\chi_{12} = \frac{v_1}{RT}(\delta_1 - \delta_2)^2 \tag{6}$$

Thus, for regular solutions, it is possible to use the solubility parameters to get a quantitative thermodynamic description from the Flory–Huggins model. For solutions containing polar and hydrogen-bonding compounds, however, Eq. (6) yields poor results [3]. It would therefore be desirable to use the Hansen

Table 1
The number of systems and data points used in the calculations

Polymer	Non-polar solvents		Polar solvents		Hydrogen-bonding solvents	
	N_{sys}	N_{DP}	N_{sys}	N_{DP}	N_{sys}	N_{DP}
PBMA	9	60	4	12	6	40
PEMA	4	5	2	6	4	10
PMA	5	17	2	6	2	4
PMMA	5	17	3	10	3	21
PVAc	7	103	4	30	2	17
Total	30	202	15	64	17	92

Table 2
Hansen solubility parameters for various polymers and calculated optimum values of the correction constant α_{opt} and average absolute deviations in percent (%AAD) at α_{opt}

Polymer	δ_d	δ_p	δ_{hb}	δ_{total}	Method	Reference	Volume		Segment		Free volume	
							α_{opt}	%AAD	α_{opt}	%AAD	α_{opt}	%AAD
PBMA	15.9	5.5	5.9	17.8	?	[4]	0.85	24	1.00	23	0.50	28
	18.0	**8.4**	**3.1**	20.1	s	[12]	0.55	19	0.75	18	0.35	24
	17.7	5.8	4.0	19.1	v	[12]	0.75	17	0.95	21	0.50	22
	17.7	1.2	6.2	18.8	e	[13]	0.90	16	1.00	22	0.60	20
PEMA	16.5	8.7	5.0	19.3	?	[4]	0.85	38	1.00	46	0.40	30
	17.6	**9.6**	**2.5**	20.2	s	[14]	0.55	39	0.55	48	0.10	31
	18.1	6.0	3.3	19.4	v	[12]	0.60	39	0.75	47	0.20	31
	17.5	1.3	7.1	18.9	e	[13]	0.95	30	1.00	41	0.65	26
PMA	**17.1**	**1.5**	**8.4**	19.1	e	[13]	0.80	28	1.00	33	0.15	36
PMMA	**18.6**	**10.5**	**7.5**	22.6	s	[4]	0.75	26	1.00	33	0.40	22
	19.1	6.5	3.9	20.5	v	[12]	0.75	22	1.00	31	0.45	18
	15.6	10.5	5.2	19.5	e	[15]	0.70	29	1.00	34	0.40	23
PVAc	17.6	2.2	4.0	18.2	?	[4]	0.30	27	0.45	34	0.05	26
	20.9	11.3	9.6	25.6	s	[14]	0.25	19	0.35	18	0.05	25
	17.6	**8.0**	**6.6**	20.4	s	[16]	0.60	19	0.90	19	0.20	24
	15.7	11.4	7.8	20.9	e	[15]	0.30	21	0.45	21	0.10	24

s: solubility measurement; v: viscosity measurement; e: estimated; ?: no information available.

Table 3
Optimum values of α and average absolute deviations (AAD) at α_{opt}, $\alpha = 0$ and $\alpha = 1$

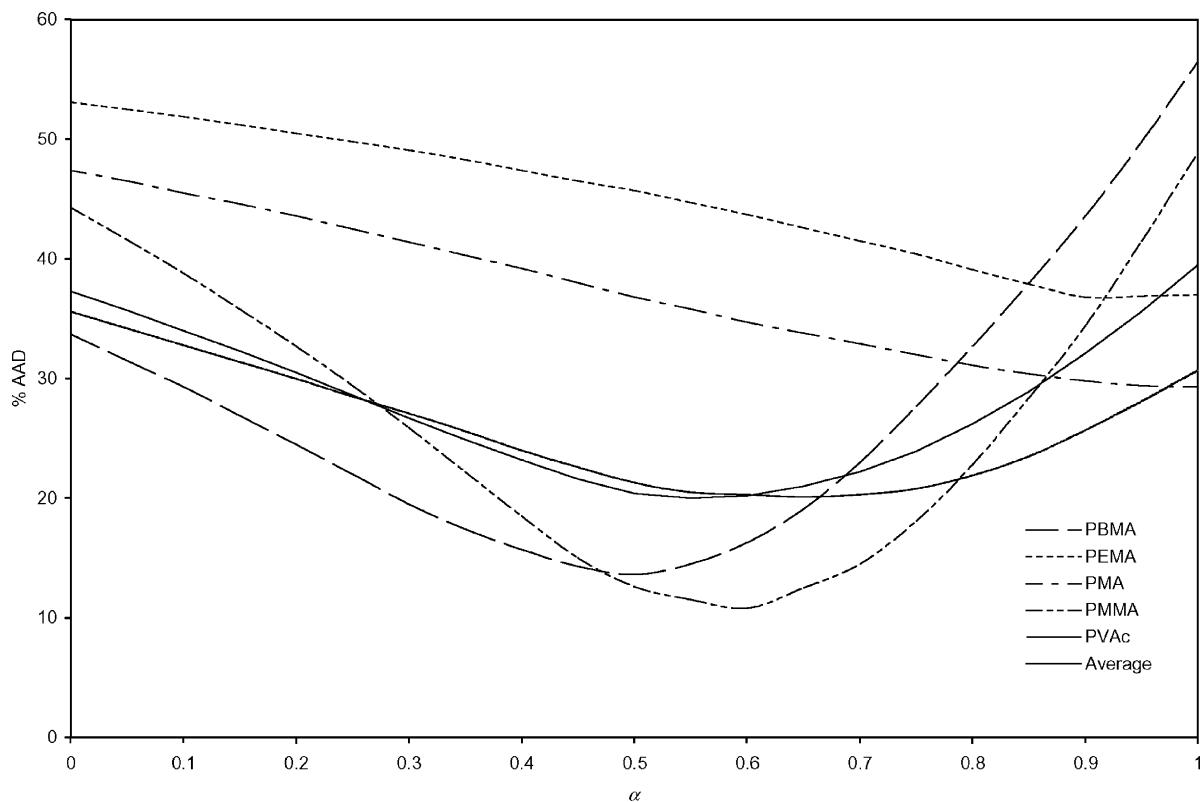| Fraction	Non-polar	Polar	Hydrogen bonding	Total
Volume				
α_{opt}	0.55	1.00	0.60	0.60
%AAD(α_{opt})	20	23	25	22
%AAD($\alpha = 0$)	37	31	54	41
%AAD($\alpha = 1$)	40	23	53	40
Segment				
α_{opt}	0.85	1.00	0.75	0.80
%AAD(α_{opt})	19	34	28	25
%AAD($\alpha = 0$)	47	48	63	51
%AAD($\alpha = 1$)	22	34	40	29
Free volume				
α_{opt}	0.25	0.05	0.40	0.30
%AAD(α_{opt})	28	20	22	26
%AAD($\alpha = 0$)	31	20	40	31
%AAD($\alpha = 1$)	76	33	87	71

Fig. 1. Influence of α on the performance of Eq. (7) for system containing non-polar solvents when the Flory–Huggins part of the model is based on volume fractions.

solubility parameters for estimating the Flory–Huggins parameters for these systems. The fact that the functionality of the Hansen solubility parameters in Eq. (3) has proven to be useful for selection of good solvents may suggest that it can also be used for estimating the Flory–Huggins parameters:

$$\chi_{12} = \alpha \frac{v_1}{RT} ((\delta_{1,d} - \delta_{2,d})^2 + 0.25(\delta_{1,p} - \delta_{2,p})^2 + 0.25(\delta_{1,hb} - \delta_{2,hb})^2) \tag{7}$$

Hansen [4] suggested to use this expression with $\alpha = 1$ and he showed that the procedure performs well, particularly for systems where dispersion forces dominate over polar and hydrogen-bonding ones. This could be anticipated, since such systems are nearly regular solutions, for which Eq. (7) with $\alpha = 1$ reduces to Eq. (6).

In a recent investigation [3], it was shown that Eq. (7) with $\alpha = 1$ combined with the Flory–Huggins model for systems containing polyacrylates, methacrylates and poly(vinyl acetate) systematically overestimates the infinite dilution solvent activity coefficients. This indicates that better results may be obtained with lower α-values. The purpose of this work is to investigate the capabilities of Eq. (7) with α estimated from experimental data and to conclude whether a universal α-value can be established for VLE calculations.
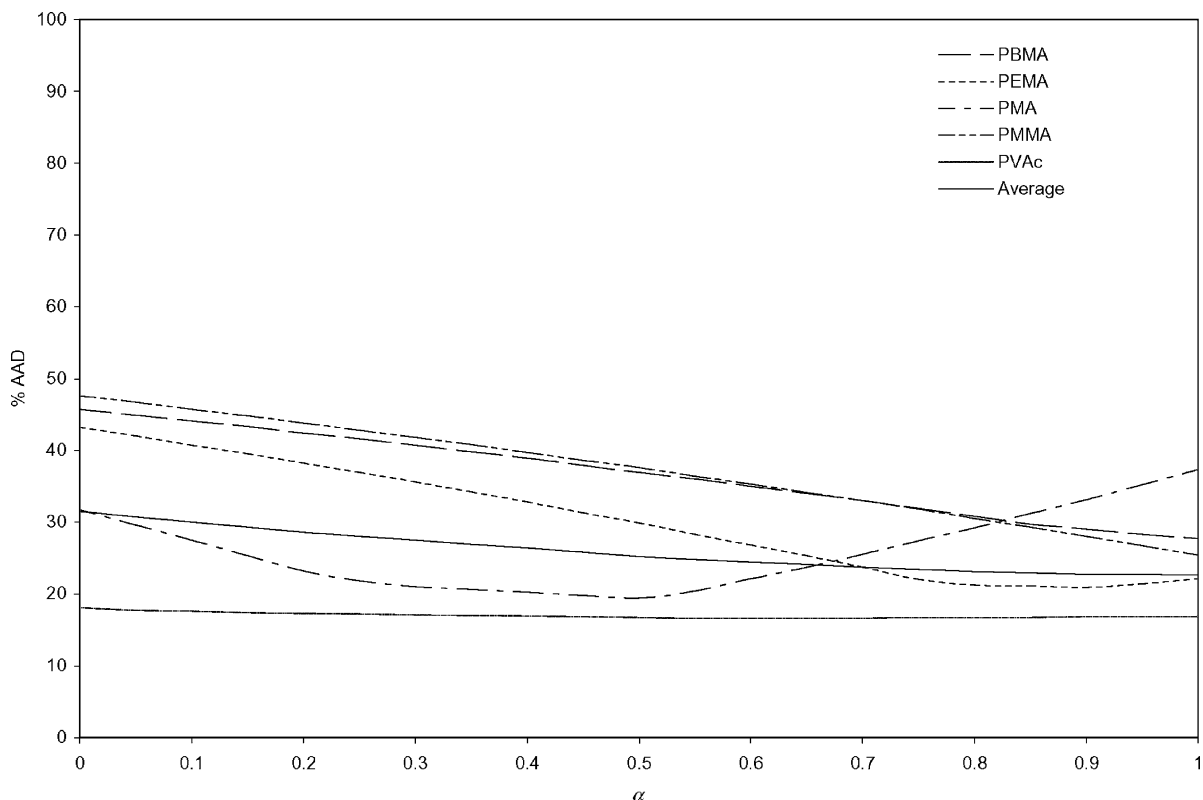

Fig. 2. Influence of α on the performance of Eq. (7) for system containing polar solvents when the Flory–Huggins part of the model is based on volume fractions.

2. Database and choice of solubility parameters

Calculation of weight fraction infinite dilution solvent activity coefficients based on various combinations of the Flory–Huggins model and Eq. (7) were performed. The Flory–Huggins combinatorial terms based on volume fractions, segment fractions and free-volume fractions were tested, and α was varied from 0 to 1.

The systems considered here are binaries containing polyacrylates, methacrylates and poly(vinyl acetate). Infinite dilution solvent activity coefficients were found in DECHEMA [5] and DIPPR [6], whereas the Hansen solubility parameters were taken from 'Hansen solubility parameters' [4] and from the *Handbook of polymer–liquid interaction parameters and solubility parameters* [7]. The number of systems and data points are listed in Table 1.

Often, several sets of solubility parameters for the same polymer exist, and in many cases they vary significantly depending on the literature source, as it can be seen in Table 2. Particularly the polar and hydrogen-bonding increments seem to be very dependent on the literature source used.

The influence of this generally observed uncertainty of Hansen solubility parameters on the performance of the models was investigated. The results are listed in Table 2.
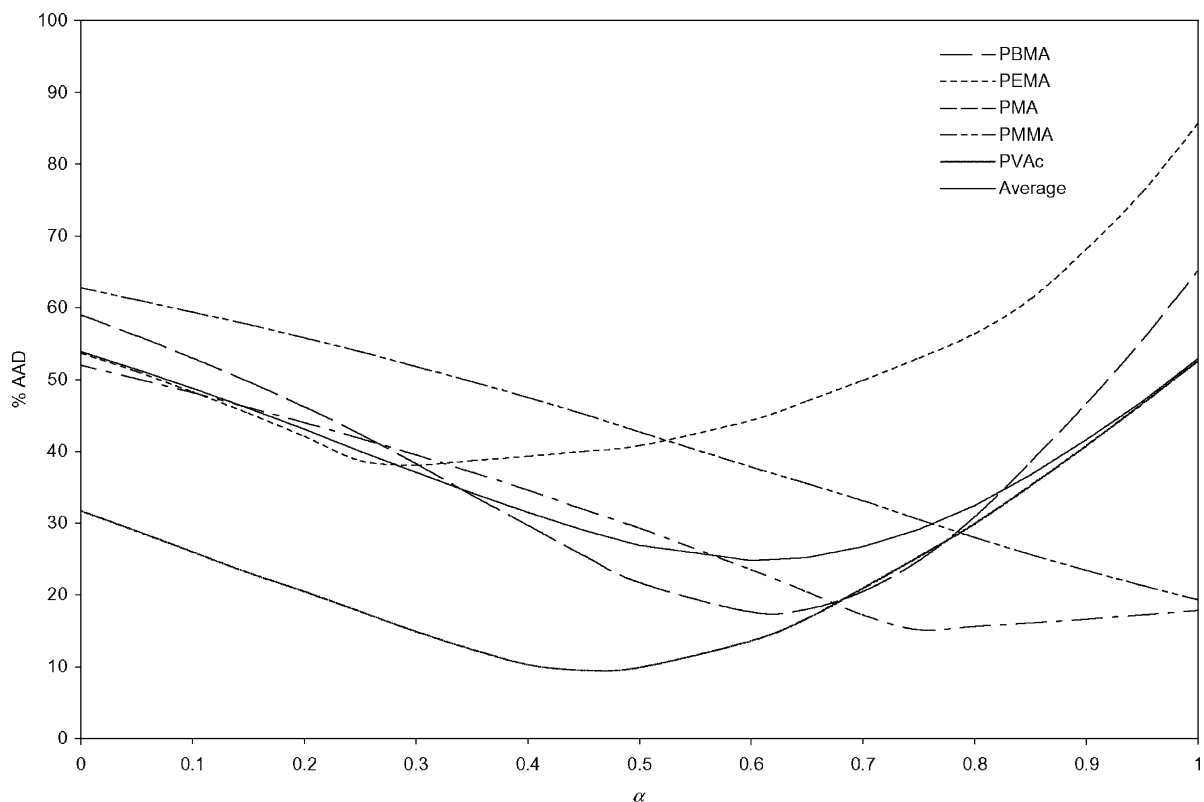

Fig. 3. Influence of α on the performance of Eq. (7) for system containing hydrogen-bonding solvents when the Flory–Huggins part of the model is based on volume fractions.

In all the cases the results depend greatly on the value of the solubility parameters used. Generally, the α_{opt} attains the highest value when used with the segment fractions and the lowest value when used with free-volume fractions. When using volume fractions, and in particular segment fractions, some entropic effects are not accounted for [2], so this obviously has to be compensated for by a higher value of α.

Thus, the results are sensitive to the solubility parameters used in the calculation. Due to the variation of the solubility parameters reported in the literature, care should be exercised when choosing what parameters to use.

We have chosen to use the parameters which have been determined by solubility measurements, since this method is supposed to be more reliable than the viscosity method [7]. Thus, in the following we have used the solubility parameters written in bold in Table 2.

3. Results and discussion

Based on the polymer Hansen solubility parameters selected in the previous section, the influence of the correction constant α on the infinite dilution solvent activity coefficients was investigated. The results are summarized in Table 3, where we have listed the locations of the minima α_{opt} and the corresponding average absolute deviations (AAD) between calculated and experimental Ω_1^∞s. All deviations are data point averages. For comparison the AAD corresponding to no residual contribution ($\alpha = 0$) and to Hansens version with $\alpha = 1$ are listed as well. The best results are obtained with α-values lower than 1, except for the polar solvents used with volume fraction and segment fraction. However, for these systems the α-dependency is very weak.

Table 4
Comparison between the performance of the Flory–Huggins/Hansen solubility parameters and group contribution models [3]

Model	%AAD
Volume-based Flory–Huggins/Hansen	22
Segment-based Flory–Huggins/Hansen	25
Free-volume-based Flory–Huggins/Hansen	26
EFV	35
UFV	39
GCF	18

The results are based on the same experimental data.

Table 5
Average absolute percentage deviations between predicted and experimental infinite dilution solvent activity coefficients for systems containing the epoxy resins Araldit 488 (10 data points) and Eponol-55 (38 data points)

Model	Araldit 488	Eponol-55
Volume-based Flory-Huggins/Hansen	31	28
EFV	34	30
UFV	119	62
GCF	29	37

The best overall results are obtained when using volume fractions, which yields an optimum value of the correction constant $\alpha = 0.6$, resulting in an AAD of 22%. A closer look at the AAD–α plots shown in Figs. 1–3 reveals that the minima for non-polar and hydrogen-bonding solvents are very close (both in terms of α_{opt} and %AAD). In Fig. 2, the aforementioned low sensitivity of the AAD to α for the polar solvents appears clearly, resulting in an AAD at the overall α_{opt} being very close to that of the other solvents.

Table 6
Prediction of PMMA solubility using various rules of thumb

Solvent	S/NS	EFV	UFV	GCF	χ_{12}	D_{12}
Hexane	NS	10.8	13.6	29.8	1.77	14.9
Toluene	S	3.2	6.4	5.8	0.74	10.7
Xylene	S	2.8	5.1	8.1	0.84	10.7
Methylene dichloride	S	3.1	7.1	3.7	0.15	4.5
Chloroform	S	1.9	2.6	1.6	0.24	7.8
Carbon tetrachloride	S	2.6	3.5	4.0	0.95	12.8
Ethylene dichloride	S	3.6	4.5	–	0.17	6.0
Trichloroethylene	S	2.5	4.4	38.4	0.37	7.9
Chlorobenzene	S	2.7	0.9	1.4	0.43	8.5
1-Chlorobutane	S	2.8	2.3	3.6	0.51	8.9
Acetone	S	10.0	16.5	8.9	0.18	6.3
MEK	S	7.9	12.3	7.2	0.20	6.0
MIBK	S	6.3	9.4	5.9	0.58	8.7
2-Heptanone	S	5.7	8.0	6.0	0.50	7.7
3-Heptanone	NS	5.2	6.0	4.7	0.56	8.1
4-Heptanone	NS	5.2	2.8	5.7	0.53	7.9
Diisopropyl ketone	NS	4.1	4.9	–	–	–
2-Octanone	NS	5.4	7.4	6.0	–	–
Ethyl acetate	S	6.6	8.4	5.3	0.36	1.7
Amyl acetate	NS	6.2	8.7	5.5	0.78	9.3
Methyl isobutyrate	NS	5.1	6.4	2.9	–	–
Methyl methacrylate	NS	3.5	5.6	7.6	0.49	8.9
Diethyl ether	NS	1.4	9.3	15.5	0.84	11.5
THF	S	4.6	5.9	–	0.18	6.1
1,4-Dioxane	S	4.1	5.4	158	0.40	8.5
Methanol	NS	40.2	62.7	21.3	0.67	19.3
Ethanol	NS	25.5	22.1	74.5	0.63	13.3
1-Butanol	NS	26.8	14.4	8.2	0.67	11.0
Cyclohexanol	NS	18.1	42.0	–	0.53	9.1
Ethylene glycol	NS	20.3	42.0	6.59×10^3	1.19	18.8
Propylene glycol	NS	124	–	935	1.18	56.3
1,3-Butanediol	NS	96.8	–	289	1.16	14.0
Glycerol	NS	168	–	1.05×10^3	2.15	25.0
1-Propanol	NS	16.9	17.0	10.0	0.63	11.8
Diethylene glycol	NS	223	–	991	1.11	13.9
Dipropylene glycol	NS	69.2	178	046	–	–

For EFV, UFV and GCF, the listed values are Ω_1^∞s. Flory–Huggins parameters χ_{12} are calculated from the Hansen solubility parameters, following the method proposed here with $\alpha = 0.6$. D_{12} are the solubility distances, which should be compared to the solubility radius of PMMA, $R_2 = 8.6$.

The majority of the experimental data are for systems containing PBMA and PVAc, as it can be seen from Table 1. Admittedly, the optimum values of α for these polymers contribute significantly to the optimum overall value $\alpha_{opt} = 0.6$. Both for the non-polar (Fig. 1) and hydrogen-bonding solvents (Fig. 3), the optimum values for PBMA and PVAc are close to 0.6, and the minima are quite clear, in the sense that a change of the value of α significantly affects the accuracy. For most other systems, the accuracy is far less sensitive to the value of α.

In contrast to the polar solvents, for the non-polar and hydrogen-bonding solvents the α-dependency is rather pronounced, particular at high values of α, as it is recognized in Figs. 1 and 2. For example, for the non-polar solvents, Eq. (7) with $\alpha = 1$ yields 40% AAD, which is about two times that

Table 7
Prediction of PEMA solubility using various rules of thumb

Solvent	S/NS	EFV	UFV	GCF	χ_{12}	D_{12}
Hexane	NS	9.0	10.2	15.3	1.01	11.3
Toluene	S	3.2	5.3	5.2	0.44	8.3
Xylene	S	2.1	4.4	6.8	0.54	8.6
Methylene dichloride	S	3.2	2.8	8.9	0.19	5.0
Chloroform	S	1.9	2.3	1.6	0.21	7.3
Carbon tetrachloride	S	2.5	2.7	7.5	0.56	9.8
Trichloroethylene	S	2.5	3.6	35.5	0.31	7.1
Chlorobenzene	S	2.6	3.4	2.6	0.22	6.0
o-Dichlorobenzene	S	1.3	2.7	1.9	0.15	4.7
Acetone	S	10.3	15.3	9.6	0.17	6.2
MEK	S	8.1	11.7	7.5	0.09	4.2
MIBK	S	6.3	8.5	8.7	0.27	6.0
Acetophenone	S	7.0	8.6	6.6	0.13	4.3
Methyl-*n*-propyl ketone	S	6.9	9.4	6.4	0.12	4.4
Ethyl acetate	S	6.2	7.8	5.0	0.32	7.3
Butyl acetate	S	6.5	6.9	4.9	0.50	7.9
Diethyl ether	S	5.8	7.6	13.4	0.57	9.5
THF	S	4.2	5.0	–	0.24	6.9
1,4-Dioxane	S	4.1	4.9	459	0.48	9.6
Methanol	NS	44.7	60.0	26.1	1.04	20.6
Ethanol	NS	66.7	24.6	15.4	1.06	17.3
1-Butanol	NS	27.2	14.9	7.9	1.13	14.2
Cyclohexanol	NS	20.2	18.4	2.2	0.97	12.3
Ethylene glycol	NS	195	–	9.48×10^3	1.88	23.6
Propylene glycol	NS	152	–	1.91×10^5	1.94	20.9
1,3-Butanediol	NS	115	–	362	1.99	19.1
Glycerol	NS	208	–	1.42×10^3	3.22	26.9
Isopropanol	NS	21.8	18.5	19.0	1.02	14.8
Dipropylene glycol	NS	86.5	323	187	–	–
Nitromethane	NS	13.8	15.3	–	0.34	10.2
1-Nitropropane	NS	4.5	1.4	–	0.11	4.5

For EFV, UFV and GCF, the listed values are Ω_1^∞s. Flory–Huggins parameters χ_{12} are calculated from the Hansen solubility parameters, following the method proposed here with $\alpha = 0.6$. D_{12} are the solubility distances, which should be compared to the solubility radius of PEMA, $R_2 = 10.4$.

obtained at α_{opt} and similar to the performance of the pure combinatorial contribution with $\alpha = 0$ (41% AAD). This shows that Flory–Huggins parameters may well be estimated from Hansen solubility parameters, but the method suggested by Hanson [4], i.e. Eq. (7) with $\alpha = 1$, is not adequate for these systems.

Table 8
Prediction of PBMA solubility using various rules of thumb

Solvent	S/NS	EFV	UFV	GCF	χ_{12}	D_{12}
Hexane	NS	7.1	7.0	10.7	0.94	10.9
n-Octane	NS	6.7	6.3	11.4	1.04	10.3
n-Decane	NS	6.5	6.1	10.7	1.20	10.0
n-Dodecane	NS	6.6	1.0	16.3	1.33	9.8
n-Hexadecane	NS	6.8	6.1	13.2	1.63	9.6
Toluene	S	3.8	4.4	4.7	0.32	7.1
Xylene	s	2.3	3.6	5.7	0.41	7.4
Methylene dichloride	S	3.3	2.5	3.0	0.10	3.7
Chloroform	S	1.9	9.1	1.7	0.14	5.9
Carbon tetrachloride	S	2.2	7.2	9.9	0.45	8.8
Ethylene dichloride	S	3.5	3.0	–	0.02	2.0
Trichloroethylene	S	2.5	2.9	23.2	0.20	5.7
Chlorobenzene	S	2.5	3.0	6.0	0.14	4.7
o-Dichlorobenzene	S	1.3	2.5	2.7	0.07	3.2
Acetone	S	10.2	14.1	11.1	0.20	6.7
MEK	S	8.4	10.5	6.2	0.11	4.5
MIBK	S	6.3	7.7	5.7	0.27	6.0
Acetophenone	S	8.1	9.3	8.6	0.08	3.3
Ethyl acetate	S	6.7	6.7	5.0	0.27	6.8
Butyl acetate	S	5.5	5.1	4.5	0.41	7.2
Diethyl ether	S	5.2	5.8	11.5	0.53	9.1
THF	S	3.8	4.0	–	0.18	6.1
1,4-Dioxane	S	4.1	4.4	159	0.34	8.1
Methanol	NS	23.7	57.7	35.7	1.03	20.4
Ethanol	NS	29.2	31.3	42.3	1.01	16.9
1-Butanol	NS	18.1	17.1	8.1	1.03	13.6
Cyclohexanol	NS	24.3	70.1	3.0	0.82	11.3
Ethylene glycol	NS	33.1	105	1.59×10^4	1.81	23.1
Propylene glycol	NS	213	–	1.18×10^3	1.85	20.4
1,3-Butanediol	NS	959	–	526	1.90	18.7
Glycerol	NS	295	–	8.88×10^3	3.11	26.5
Isopropanol	NS	23.7	21.6	10.6	0.94	14.2
Isobutanol	S	99.0	17.9	3.5	1.17	14.3
Diethylene glycol	NS	240	–	2.47×10^3	1.91	18.2
Dipropylene glycol	NS	128	946	258	–	–
Nitromethane	NS	16.7	14.2	–	0.43	11.5
1-Nitropropane	S	4.7	5.2	–	0.16	5.4
N,*N*-Dimethylformamide	S	3.8	–	–	0.45	9.8

For EFV, UFV and GCF, the listed values are Ω_1^∞s. Flory–Huggins parameters χ_{12} are calculated from the Hansen solubility parameters, following the method proposed here with $\alpha = 0.6$. D_{12} are the solubility distances, which should be compared to the solubility radius of PBMA, $R_2 = 8.5$.

Generally, the performance of the Flory–Huggins/Hansen solubility parameter model used with the optimum value of α is good, particularly when taken into consideration that the experimental data often may be associated with uncertainties up to 20% [8].

In a recent publication, the group-contribution models EFV, UFV and GCF were investigated for the same systems as those of this work [3]. The overall results are compared with the results from the Flory–Huggins/Hansen solubility parameter models in Table 4, which indicate that the method proposed here performs better than EFV and UFV and similar to GCF for the systems investigated here.

For many commercial paint resins, Hansen solubility parameters are available, but their molecular structures are not. Group-contribution methods require knowledge of the molecular structure of all the constituents of the systems to be considered, i.e. they can not be used for many commercially important paint systems. The proposed volume-based method only requires the knowledge of the Hansen solubility parameters and the densities. Thus, this model may provide a first tool for phase equilibria calculations for systems containing complex paint resins of unknown structure.

The model was finally tested for its predictive capabilities, so in the following we consider systems, which were not included in the evaluation of the α-parameter. We employ the Flory–Huggins/Hansen solubility parameter model for calculations of the infinite dilution solvent activity coefficients for systems

Table 9
Prediction of PVAc solubility using various rules of thumb

Solvent	S/NS	EFV	UFV	GCF	χ_{12}	D_{12}
Hexane	NS	38.7	38.6	30.4	1.09	11.7
Toluene	S	2.6	8.0	1.6	0.42	8.1
Chloroform	S	0.1	1.2	1.7	0.10	5.0
Carbon tetrachloride	NS	3.3	4.2	5.3	0.59	10.0
Ethylene dichloride	S	2.7	2.7	–	0.06	3.6
Chlorobenzene	S	3.8	3.7	2.0	0.26	6.5
Acetone	S	5.6	6.8	7.3	0.11	4.9
MEK	S	5.4	6.5	6.3	0.07	3.7
MIBK	NS	6.5	7.8	6.0	0.24	5.6
3-Heptanone	NS	8.5	9.4	6.3	0.20	4.8
Diisobutyl ketone	NS	15.3	10.2	4.4	0.38	5.9
Ethyl acetate	S	4.8	4.8	5.2	0.12	4.5
Butyl acetate	S	6.0	5.8	6.2	0.25	5.6
Diethyl ether	NS	11.4	10.5	16.5	0.42	8.2
THF	S	8.4	5.6	–	0.05	3.1
1,4-Dioxane	S	4.2	3.3	117	0.24	6.9
Methanol	S	18.9	19.4	12.7	0.71	17.0
Ethanol	NS	15.2	38.9	14.3	0.63	13.3
1-Butanol	NS	14.7	11.1	9.2	0.56	10.0
Cyclohexanol	NS	8.4	6.6	–	0.40	7.9
Ethylene glycol	NS	7.4	6.3	5.10×10^3	1.31	19.7
Diethylene glycol	S	27.8	–	736	1.26	14.8
Dipropylene glycol	S	27.3	213	123	–	–
Nitromethane	S	3.9	3.8	–	0.43	11.5

For EFV, UFV and GCF, the listed values are Ω_1^∞s. Flory–Huggins parameters χ_{12} are calculated from the Hansen solubility parameters, following the method proposed here with $\alpha = 0.6$. D_{12} are the solubility distances, which should be compared to the solubility radius of PVAc, $R_2 = 4.1$.

Table 10
Validity of the solubility answers obtained from five methods for solvent screening

Model	Correct	Incorrect	No answer	No calculation
Volume-based Flory-Huggins/Hansen	102	20	–	7
Original Hansen	99	23	–	7
EFV	91	19	19	0
UFV	78	21	17	13
GCF	72	26	14	17

No answer is obtained from the Ω_1^∞ rule of thumb when the value of Ω_1^∞ is between 6 and 8. Hansen solubility parameters were unavailable for a few components, and no calculation was performed.

containing the commercial epoxy resins Araldit 488 and Eponol-55 and for screening for suitable solvents for acrylate and acetate resins at room temperature. The performance of the method is compared to the results from the group-contribution models EFV, UFV and GCF, which have been published previously [3].

As mentioned before, the proposed method is particularly attractive for systems containing paint related resins, since often their molecular structure is unavailable, which make most alternative methods, as those based on group-contribution, impossible to use. For the epoxy resins Araldit 488 and Eponol-55, as an exception the molecular structure is known [3], so in this case a comparison with the group-contribution methods is possible. The experimental data were those published by Newman and Prausnitz [9] and Alessi et al. [10], and the results are shown in Table 5. For this application, the volume-based Flory–Huggins/Hansen solubility parameter model is slightly better than GCF and EFV and much better than UFV.

According to the Flory–Huggins model a polymer and solvent are completely miscible if $\chi_{12} <$ $0.5(1 + \sqrt{v_1/v_2})^2 \simeq 0.5$, so the proposed volume-based model can be used for screening for suitable solvents. Group-contribution models can also be used for fast screening if used with an empirical rule of thumb, which states that complete miscibility is obtained when the value of the infinite dilution solvent activity coefficient is below 6, whereas at values above 8, phase separation occurs at some concentration range [11]. This rule of thumb was recently shown to yield good results for systems containing the same polymers as investigated in this work [3].

In Tables 6–9, we have demonstrated the result of a solvent screening investigation for PMMA, PEMA, PBMA and PVAc at 25 °C based on the aforementioned methods, and in Table 10 the overall performance is compared, from which it appears that the proposed method yields approximately the same number of correct solubility indication as the original Hansen solubility parameter model and EFV for these systems.

4. Conclusions

We have developed a Flory–Huggins type model, which permits direct use of the existing Hansen solubility parameters. The following conclusions can be drawn from the work:

- Hansen solubility parameters can be used for estimating the Flory–Huggins parameters for systems containing PBMA, PEMA, PMA, PMMA and PVAc. The method is based on a modified Hansen expression, which includes a universal correction factor.

- The method is sensitive to the variation of the Hansen solubility parameters often seen in the literature.
- The method performs similarly and often better than the group-contribution models EFV, UFV and GCF when used in a predictive manner for calculation of activity coefficients of solvents infinitely diluted in the commercial paint resins Araldit 488 and Eponol-55 and for screening for suitable solvents for acrylate and acetate resins at room temperature. However, unlike the group-contribution models, knowledge of the molecular structure of the compounds of interest is not required; the only inputs in the proposed Flory–Huggins/Hansen model are the pure-component densities and Hansen solubility parameters.

List of symbols

D Solubility distance in Hansen 3D plots (MPa$^{1/2}$)
N Number of systems and data points
R Radius of solubility sphere in Hansen 3D plots (MPa$^{1/2}$)
u Internal energy (J/mole)
v Molar volume (cm^3/mole)
x Mole fraction

Greek letters

γ Molar-based activity coefficient
Δ Change of property
δ Solubility parameter ((J/cm^3)$^{1/2}$)
ϕ Volume fraction
χ Flory–Huggins parameter
Ω Weight fraction based activity coefficient

Subscripts

1   Component index for the solvent
2   Component index for the polymer
DP   Data points
hb   Hydrogen bonding
i Component index
np   Non-polar
p   Polar
sys   Systems
vap   Vaporization

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