Thermodynamics of Paint-Related Systems with Engineering Models

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Paints are complex materials composed of polymers (binders) dissolved in one or more solvents, pigments, and other additives. The thermodynamics of such systems is essential, for example, for selecting improved solvents and understanding a number of phenomena related especially to adhesion to solid surfaces and drying. Many engineering models have been applied over the last decades for solutions with commoditity polymers. In this work, the performance of some of these models is investigated for paint-related systems, focusing on those drying by the so-called "lacquer mechanism" (evaporation of solvents). These are the Entropic-FV, UNIFAC-FV, GC-Flory, and the Flory-Huggins models using various ways for estimating the FH parameter via solubility parameters. Achievements and shortcomings of these models are discussed in conjunction with difficulties encountered in such calculations. We conclude that, despite the uncertainties involved, several models yield reasonably accurate activity coefficients, even at infinite dilution. Thus, engineering models may be useful for solvent selection via semiempirical rules of thumb, which are based on thermodynamic considerations.

Introduction

Paints are complex multicomponent materials. Typical binders employed by the Danish Paint Industry are acrylics, epoxies, phenolics, and alkyds. The proper choice of solvent is considered crucial for both economic and environmental reasons. The latter become increasingly more important with the pressure for substituting or reducing the volatile organic content (VOC) of paints. Besides for solvent selection, polymer thermodynamics serves numerous roles in the paint industry, especially in understanding the interactions between the paint film and various species inside and outside the paint (additives, pigments, external solvents, and vapors), the drying process of the paint film, the adhesion of paint on various surfaces, and so on (Funke, 1997; Holten-Andersen and Eng, 1988).

Basic thermodynamic relationships apply, in principle, for the systems employed in paints. However, the complexity of paints and coatings compared to systems related to plastics and other engineering polymers (polyolefins, polystyrene, PVC) are due to the following:

- Mixed solvents are typically employed, but most literature data and theoretical investigations (models) are confined to single solvent–polymer systems.
- The effect of a large number of interactions needs to be considered. Traditional models typically present problems for such multicomponent systems.
- Most binders are of a rather complex chemical structure, and a number of different functional groups (such as hydroxyl, amine, acetate) are involved. Often several such groups appear in a single paint binder, for example, in epoxies.
- Most organic solvents employed for paints possess polar groups or groups capable of hydrogen bonding.

The preceding factors can create problems when existing models are used for paint-related polymer systems. Traditionally, in the paint and coatings industry, the three-dimensional (3-D) solubility parameter concept proposed by Hansen (Bentley and Turner, 1998; Hansen, 2000) is used for solvent selection. The method provides a very useful rule of thumb for fast calculations. It is, however, empirical, it requires experimental data, it does not account for concentration and molecular weight effects, and provides only yes/no answers.

Since 1970, a wealth of thermodynamic concepts have developed, which may be very relevant to paint research. Among them, of special importance are the group-contribution concept, the association theories for hydrogen-bonding systems,

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Table 1. Thermodynamic Models in the Polymers Plus Software Package

Activity Coefficient	Equations of State
Flory-Huggins	Sanchez-Lacombe
Polymer-NRTL	SAFT
UNIFAC-FV	Polymer-SRK

and the possibility of employing simple cubic equations of state (EoS) for polymers.

Among the models, those based on group-contributions can be particularly useful for paints and coatings due to the variety of solvents and polymers involved in the paint industry. Such models have already gained some acceptance in the traditional polymer industry (Bokis et al., 1999).

The purpose of this work is the following. First to investigate the applicability of a number of engineering models in predicting infinite dilution solvent activity coefficients for polymer–solvent systems of relevance to the paint and coatings industry. These systems include acrylates, acetates, and epoxies. Further, to evaluate the possibility of using the Hansen solubility parameters, employed currently independently in the paint industry, in combination with the Flory-Huggins model. Finally, to apply the best models for solvent selection using semiempirical rules of thumb.

Many reviews of the numerous thermodynamic models for systems containing polymers have been given in the literature (Goydan et al., 1989; Fried et al., 1992; Danner and High, 1993; Bogdanic and Fredenslund, 1995; Condo and Radosz, 1996; Lee and Danner, 1997; Bokis et al., 1999), showing that the accuracy depends on the type of equilibrium and system to be considered. Thus, the best model chosen for a particular application by the practicing engineer will depend on the problem to be solved. In their recent review article, Bokis et al. (1999) listed the models currently supplied in the Polymer Plus software package. These are shown in Table 1.

At this stage, we could mention that a successful model for paints and coatings:

- Should be applicable to both VLE and LLE for binary and multicomponent systems
- Primarily needs to be successful at low pressures
- Should be predictive, that is, contain a parameter table for a large range of interactions (group or molecular)
- Should be applicable to hydrogen-bonding systems.

Based on these requirements and the available models, we have chosen to evaluate at this stage:

- Three activity coefficient models: the Flory-Huggins (Flory, 1942; Huggins, 1942), Entropic-FV (Elbro et al., 1990; Kontogeorgis et al., 1993), and UNIFAC-FV (Oishi and Prausnitz, 1978).
- One equation of state: the GC-Flory model (Chen et al., 1990; Bogdanic and Fredenslund, 1994).

We refer to the original publications for a detailed description of the models. It should be emphasized, however, that all models are predictive. All models, except for the Flory-Huggins model, are group-contribution models with parameters estimated from VLE-data for low molecular-weight compounds. In this work, the Flory-Huggins model was also made predictive by estimating the Flory-Huggins parameter from solubility parameters, either using the original Hildebrand parameters:

$$\chi_{12} = \frac{v_1}{RT}(\delta_1 - \delta_2)^2 \tag{1}$$

or the Hansen 3-D solubility parameters (Hansen, 2000):

$$\chi_{12} = \frac{v_1}{RT}\left[(\delta_{d1} - \delta_{d2})^2 + 0.25(\delta_{p1} - \delta_{p2})^2 + 0.25(\delta_{h1} - \delta_{h2})^2\right]. \tag{2}$$

Model Evaluation and Treatment of Specific Problems

The performance of the models has been investigated by considering the weight based activity coefficient at infinite dilution:

$$\Omega_i = \frac{a_i}{w_i} = \frac{\gamma_i x_i}{w_i}. \tag{3}$$

Infinite dilution data for polymer-solvent systems are available in the literature. These data have been collected in two major databases available by DIPPR (Danner and High, 1993) and DECHEMA (Wen et al., 1991). Experimental uncertainties may be high, up to 30% (Lee and Danner, 1996a–c, 1997).

The molar volume needed by EFV and UFV is available in the literature for many polymers, often in the form of the Tait correlation (in the following we refer to molar volumes just as volumes). The parameters by Rodgers (1993) have been used in this work. However, as recognized by Pappa et al. (1999), the volume of poly(*n*-butyl methacrylate) as given by Rodgers's parameters, yields an absolute average deviation from experimental data of 6.8%. Hence, the new Tait parameters by Pappa et al. (1999) have been used in this work.

The polymers considered in this work are polyacrylates and -methacrylates, poly(vinyl acetate), and epoxies. Except for poly(vinyl acetate), these polymers cannot be treated by the two-activity-coefficient models in a straightforward manner. In standard UNIFAC tables the atomic groups CHCOO and CCOO are lacking (Hansen et al., 1992). Paints polymers, as for example, polyacrylates and -methacrylates, often contain exactly these groups. Due to the relevance of this issue, a thorough discussion has been given in the Appendix, which points out the importance of dividing these polymers into appropriate atomic groups. For CHCOO and CCOO, it is recommended to use the acetate main-group interaction parameters and the physical R- and Q-parameters calculated from the bond-lengths given by Bondi (1968).

For many paint-related systems, two additional problems exist: the molecular structure of the polymer (repeating unit) and its experimental volume are not available. In this work, these problems have been confronted for two commercial epoxies (Eponol-55 and Araldit 488). This will be outlined in the following.

Molecular structure of epoxies

Experimental activity coefficient data for some commercial resins have been reported in the literature (Newman and

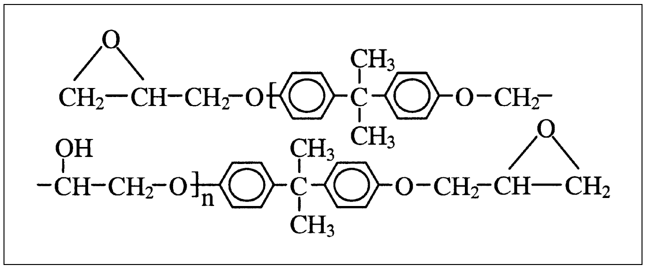

Figure 1. Molecular structure of commercial epoxies Eponol-55 and Araldit 488.

The *n*-values for the two resins are different and were provided by Dr. Meijer and Prof. Kikic.

Prausnitz, 1973; Alessi et al., 1978). Still, the exact molecular structure has been reported in none of the cases. Knowing the molecular structure, though, is crucial for group-contribution models. The exact structure of the resins Eponol-55 (Shell Chemical Co.) and Araldit 488 (Ciba) has been established through personal correspondence (H. Meijer, Shell Research, Amsterdam; I. Kikic, University of Trieste). The structure is shown in Figure 1.

Volumes of the epoxies

Free volume activity coefficient models require the experimental volumes as a parameter. For many paint-related polymers these are not available, for example, for Eponol-55 and Araldit 488. Two methods suitable for estimating the polymer density have been considered: the GC-vol (Elbro et al., 1991) and the van Krevelen methods (van Krevelen, 1990).

In GC-vol we need extra group volume parameters for the aromatic carbon AC. For this group, the GC-vol parameters were calculated to be $A_{AC} = 3.65$ cm^3/mol, $B_{AC} = -15.27 \times 10^{-3}$ cm^3/(mol·K), and $C_{AC} = 0$.

Activity coefficients of solvents at infinite dilution in Araldit 488 and Eponol-55 have been estimated by using the GC-vol and the van Krevelen methods. In Table 2 the results are compared with the experimental data listed in the DIPPR and DECHEMA databases. The calculation results are based on 23 systems and 51 data points.

Using the volumes from van Krevelen, UFV yields results that are somewhat better than EFV. Using the volumes from GC-vol, EFV yields slightly better results, whereas the results from UFV are getting clearly worse. This shows that UFV is more sensitive to volume than EFV. Since volumes need to be estimated for many paint-related polymers, this is a clear disadvantage of UFV as compared to EFV.

Table 2. Average Absolute Deviation in %: Experimental vs. Calculated Solvent Activity Coefficients at Infinite Dilution for Systems Containing Araldit 488 and Eponol-55

Polymer	V-Method	EFV	UFV	GCF
Araldit 488	GC-vol	34	119	29
Eponol-55	GC-vol	30	62	37
Araldit 488	van Krevelen	43	35	29
Eponol-55	van Krevelen	34	28	37

Note: The polymer volumes have been estimated with the GC-vol and van Krevelen methods.

Table 3. Average Absolute Deviation in %: Calculated vs. Experimental Infinite Dilution Activity Coefficients of Nonpolar Solvents in Acrylates

Polymer	N_{sys}	N_{DP}	EFV	UFV	GCF
PBMA*	11	60	22	22	11
PEA	2	2	45	54	36
PEMA**	4	5	47	49	36
PMA†	5	17	45	46	28
PMMA	5	17	40	25	26
PVAc††	8	103	20	19	17
Total	35	204	26	24	17

*For GCF 50 data points.
**For GCF 4 data points.
‡For GCF 12 data points.
††For GCF 93 data points.

Table 4. Average Absolute Deviation in %: Calculated vs. Experimental Infinite Dilution Activity Coefficients of Polar Solvents in Acrylates

Polymer	N_{sys}	N_{DP}	EFV	UFV	GCF
PBMA*	4	12	9	13	11
PEA	1	1	15	22	27
PEMA	2	6	10	11	11
PMA	2	6	35	36	25
PMMA	3	10	25	25	23
PVAc**	4	30	36	25	24
Total	16	65	26	23	21

*For GCF 9 data points.
**For GCF 27 data points.

Results and Discussions

In this section we will present the results as follows: first those obtained from the three group-contribution models and then the results from various Flory-Huggins/solubility-parameter models. Finally, we have investigated a rule of thumb for the selection of solvents for paint resins. The theory behind this rule of thumb, how to evaluate it, and the results are presented in the last subsection.

Results obtained from the group-contribution models

Calculated and experimental solvent activity coefficients at infinite dilution in those polymers for which volumes are available are presented in Tables 3, 4 and 5. The absolute average deviation between calculated and experimental values, the number of systems, and the number of data points

Table 5. Average Absolute Deviation in %: Calculated vs. Experimental Infinite Dilution Activity Coefficients of Solvents Capable of Forming Hydrogen Bonds in Acrylates.

Polymer	N_{sys}	N_{DP}	EFV	UFV	GCF
PBMA	6	40	65	87	24
PEMA	3	10	46	47	21
PMA	2	4	16	34	9
PMMA	3	21	108	117	12
PVAc	2	17	15	63	15
Total	16	92	61	83	19

are listed for each type of solvent, that is, nonpolar, polar, and hydrogen bonding solvents.

For systems containing cyclohexane or cyclohexanone it was not possible to perform calculations with the GCF model. This is due to the fact that no liquid root exists. This is a limitation of the model, which can be solved with revised parameters.

For nonpolar and polar solvents all models yield reasonably good results, the GCF-model being the most accurate one.

For the hydrogen-bonding solvents, GCF is again the best model. In this case GCF clearly performs better than the two activity coefficient models, of which the UFV yields significanly worse results than EFV.

It seems that GCF performs equally well for all types of systems, with an average deviation from experimental results for the hydrogen-bonding systems being very similar to those of the less "difficult" systems (nonpolar and polar solvents). This is in contrast to EFV and UFV, both of which perform significantly worse for the systems containing hydrogen-bonding components than other solvents. This may indicate that the UNIFAC parameters related to COOH and OH (present in all of the hydrogen-bonding solvents) are not optimum for this application.

In the evaluation of the models for systems containing epoxy resins we also included calculations from GCF. These results were shown in Table 2. The performance of GCF is similar to that of EFV. The advantage of GCF for these systems is that the volumes of the epoxy resins are not required.

Results obtained from the Flory-Huggins/solubility-parameter models

The combinatorial contribution in Flory-Huggins theory has proved valuable in the description of the entropic effects associated with differences in size and shape, but it does not take into account the contribution from free volume differences. Using free volume fractions (as in EFV) instead of volume fractions was shown to give a more accurate nonenergetic contribution to the activity coefficient (Elbro et al., 1990). Thus, in addition to the Flory-Huggins/solubility-parameter approach based on volume fraction, it would be interesting to investigate the approach based on free volume fractions.

Calculations have been performed with the following four different versions of the Flory-Huggins/solubility-parameter approach:

- Flory-Huggins based on volume fractions/Hildebrand solubility parameters (VHi)
- Flory-Huggins based on free volume fractions/Hildebrand solubility parameters (FVHi)
- Flory-Huggins based on volume fractions/Hansen solubility parameters (VHa)
- Flory-Huggins based on free volume fractions/Hansen solubility parameters (FVHa).

The results are shown in Tables 6, 7 and 8. These results are based on the same systems as the calculations made with the group contribution models.

Very large deviations (thousands of percent) were obtained for the PEA/hexane system. The deviations are all caused by unrealistically high energetic contributions to the activity coefficient, that is, the solubility parameters used may be associated with errors. The calculated results for the PEA/hexane system have therefore been excluded from the calculated total deviations for the nonpolar systems.

For the nonpolar solvents: based on the volume fractions, the Hansen solubility parameters (VHa: 33% average absolute deviation) work better than the Hildebrand parameters (VHi: 42%). However, when the free volume fractions are used, the Hildebrand parameters perform better (FVHi: 33%), whereas the Hansen parameters perform worse (FVHa: 47%). The same picture is observed for polar solvents.

The picture changes slightly for hydrogen-bonding solvents, for which volume fractions work better than free volume fractions for both types of solubility parameters.

We conclude that FVHi is the most accurate of the four models for nonpolar and polar systems. The accuracy in these systems is comparable to that of the two group-contribution models EFV and UFV. For the hydrogen-bonding systems FVHi is still as accurate as the two activity coefficient mod-

Table 6. Average Absolute Deviation in %: Calculated vs. Experimental Infinite Dilution Activity Coefficients of Nonpolar Solvents

Polymer	VHi	FVHi	VHa	FVHa
PBMA	39	20	16	59
PEA	163	322	69	171
PEMA	54	48	38	50
PMA	60	42	60	42
PMMA	16	62	17	114
PVAc	44	31	41	29
Total	42	33	33	47

Note: The number of systems and data points is the same as in Table 3.

Table 7. Average Absolute Deviation in %: Calculated vs. Experimental Infinite Dilution Activity Coefficients of Polar Solvents

Polymer	VHi	FVHi	VHa	FVHa
PBMA	53	25	52	22
PEA	18	44	30	23
PEMA	59	19	55	22
PMA	48	20	48	20
PMMA	45	34	50	21
PVAc	34	21	19	84
Total	43	24	36	50

Note: The number of systems and data points is the same as in Table 4.

Table 8. Average Absolute Deviation in %: Calculated vs. Experimental Infinite Dilution Activity Coefficients of Solvents Capable of Forming Hydrogen Bonds

Polymer	VHi	FVHi	VHa	FVHa
PBMA	35	81	25	29
PEMA	34	43	43	56
PMA	62	36	62	36
PMMA	58	17	37	32
PVAc	43	111	112	210
Total	43	65	47	67

Note: The number of systems and data points is the same as in Table 5.

els. However, it is no longer the most successful of the four Flory-Huggins/solubility-parameter models. GCF performs better than the Flory-Huggins/solubility-parameter models for all systems.

As mentioned earlier, free volume fractions account more satisfactorily for the nonenergetic effects than volume fractions (Elbro et al., 1990). The fact that the change from volume fractions to free volume fractions leads to worse results in the Flory-Huggins/Hansen solubility-parameter approach indicates that the Hansen solubility parameters may not account only for the energetic effects for the systems investigated here.

Rule of thumb for choosing solvents for paint binders

Direct choice of suitable solvents requires liquid–liquid equilibrium (LLE) calculations. LLE will provide us with the whole phase boundary as a function of temperature, concentration, and polymer molecular weight. However, as shown by many researchers, predictive models, such as Entropic-FV and GC-Flory, yield only qualitatively satisfactory results for LLE, even for moderately complicated polymer solutions (Kontogeorgis et al., 1995; Saraiva et al., 1995). The same models are more satisfactory for VLE and infinite dilution activity coefficients, as shown for paint systems in the previous section. Since a yes/no answer is often adequate, it is highly advantageous to employ rules of thumb for solvent selection based exclusively on the knowledge of the solvent activity coefficient at infinite dilution. Such rules of thumb have been previously proposed by several researchers (Holten-Andersen and Eng, 1988; Elbro, 1992; Klein and Jeberien, 1980). They are usually derived from the Flory-Huggins model.

Complete miscibility requires that the activity of each component is a monotonically increasing function of its concentration:

$$\frac{da_1}{dw_1} > 0 \tag{4}$$

through the entire concentration range.

Holten-Andersen and Eng (1988) showed that for the FH equation complete miscibility requires that the volume-frac-

Table 9. Prediction of PMMA Solubility Using Hansen Solubility Parameters and Group Contribution Models with the Ω_1^∞-Rule of Thumb

Solvent	s/ns	EFV	UFV	GCF	FVHi	D_{Ha}
Hexane	ns	10.8	13.6	29.8	123	14.9
Toluene	s	3.2	6.4	5.8	9.7	10.7
Xylene	s	2.8	5.1	8.1	11.4	10.7
Methylene dichloride	s	3.1	7.1	3.7	6.3	4.5
Chloroform	s	1.9	2.6	1.6	2.5	7.8
Carbon tetrachloride	s	2.6	3.5	4.0	5.2	12.8
Ethylene dichloride	s	3.6	4.5	—	4.1	6.0
Trichloroethylene	s	2.5	4.4	38.4	4.3	7.9
Chlorobenzene	s	2.7	0.9	1.4	4.4	8.5
1-Chlorobutane	s	2.8	2.3	3.6	13.1	8.9
Acetone	s	10.0	16.5	8.9	5.2	6.3
MEK	s	7.9	12.3	7.2	6.6	6.0
MIBK	s	6.3	9.4	5.9	41.4	8.7
2-Heptanone	s	5.7	8.0	6.0	16.9	7.7
3-Heptanone	ns	5.2	6.0	4.7	11.9	8.1
4-Heptanone	ns	5.2	2.8	5.7	18.3	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	8.2	1.7
Amyl acetate	ns	6.2	8.7	5.5	22.0	9.3
Methyl isobutyrate	ns	5.1	6.4	2.9	—	—
Methyl methacrylate	ns	3.5	5.6	7.6	13.9	8.9
Diethyl ether	ns	1.4	9.3	15.5	37.4	11.5
THF	s	4.6	5.9	—	5.2	6.1
1,4-Dioxane	s	4.1	5.4	158	3.8	8.5
Methanol	ns	40.2	62.7	21.3	9.1	19.3
Ethanol	ns	25.5	22.1	74.5	3.2	13.3
1-Butanol	ns	26.8	14.4	8.2	4.1	11.0
Cyclohexanol	ns	18.1	42.0	—	3.7	9.1
Ethylene glycol	ns	20.3	42.0	6.59×10^3	31.7	18.8
Propylene glycol	ns	124	—	935	17.1	56.3
1,3-Butanediol	ns	96.8	—	289	13.9	14.0
Glycerol	ns	168	—	1.05×10^3	681	25.0
1-Propanol	ns	16.9	17.0	10.0	4.6	11.8
Diethylene glycol	ns	223	—	991	16.9	13.9
Dipropylene glycol	ns	69.2	178	146	—	—

Note: The solubility radius of PMMA is 8.59.

tion-based infinite dilution activity coefficient of the solvent is less than 4.5. For a mass-fraction-based activity coefficient they suggest the following guidelines:

$$\begin{array}{rll} \Omega_1^\infty < 6: & \text{Good miscibility} & \\ 6 < \Omega_1^\infty < 8: & \text{Uncertain} & (5) \\ 8 < \Omega_1^\infty: & \text{Immiscibility likely.} & \end{array}$$

Elbro (1992) showed that the rule of thumb correctly predicts the solubility of a large number of organic compounds in two isomers of poly(butyl methacrylate). Although the validity of the approach is clearly subject to the limitations of the FH model, its use for evaluating solvent–polymer miscibility is attractive for a number of reasons:

- It eliminates the need for liquid–liquid equilibrium measurements.
- It permits use of the existing large amount of solvent infinite dilution activity coeifficients.
- No model and no data reduction is required.

In the following we evaluate the rule of thumb together with the models EFV, UFV, GCF, and FVHi, since the previous sections indicated that these were the best of the models investigated. Additionally, calculations were performed with the original Hansen solubility-parameter model. According to this model a chemical is a solvent if the distance between the solvent and polymer-solubility parameter points in a $(2\delta_h, \delta_p, \delta_h)$ coordinate system,

$$D = \sqrt{4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2}, \quad (6)$$

is lower than a certain value R. Thus, all solvents are located within a sphere, with the polymer coordinates being the center and with radius R.

Experimental solvent(s)/nonsolvent(ns) data as well as θ-temperatures are available for many polymers in several sources in the literature (Gowariker et al. 1986; Elbro, 1992, Brandrup et al., 1999). In the calculations we have set the polymer molecular weight to 50,000 g/mol (Ω_1^∞ varies only slightly with the molecular weight).

Tables 9–12 present experimental solubility indications and calculated infinite dilution solvent activity coefficients at 25°C for PMMA, PEMA, PBMA, and PVAc, for which Tait volume correlations are available in the articles by Rodgers (1993) and Pappa et al. (1999). For these polymers the rule of thumb provides us with correct answers in most of the systems containing alkanes, aromatics, chlorinated compounds, and alcohols. For the systems containing ethers most of the answers obtained from GCF are wrong. Finally, for the

Table 10. Prediction of PEMA Solubility Using Hansen Solubility Parameters and Group Contribution Models with the Ω_1^∞-Rule of Thumb

Solvent	s/ns	EFV	UFV	GCF	FVHi	D_{Ha}
Hexane	ns	9.0	10.2	15.3	13.2	10.5
Toluene	s	3.2	5.3	5.2	4.0	8.4
Xylene	s	2.1	4.4	6.8	3.9	8.2
Methylene dichloride	s	3.2	2.8	8.9	4.6	4.3
Chloroform	s	1.9	2.3	1.6	1.7	6.2
Carbon tetrachloride	s	2.5	2.7	7.5	2.1	10.0
Trichloroethylene	s	2.5	3.6	35.5	2.4	6.4
Chlorobenzene	s	2.6	3.4	2.6	2.8	7.3
o-Dichlorobenzene	s	1.3	2.7	1.9	2.5	6.2
Acetone	s	10.3	15.3	9.6	4.0	3.3
MEK	s	8.1	11.7	7.5	3.9	1.1
MIBK	s	6.3	8.5	8.7	5.1	3.7
Acetophenone	s	7.0	8.6	6.6	4.0	6.3
Methyl *n*-propyl ketone	s	6.9	9.4	6.4	4.0	1.5
Ethyl acetate	s	6.2	7.8	5.0	3.7	4.3
Butyl acetate	s	6.5	6.9	4.9	4.3	5.4
Diethyl ether	s	5.8	7.6	13.4	7.7	7.1
THF	s	4.2	5.0	—	3.5	4.3
1,4-Dioxane	s	4.1	4.9	459	3.2	8.9
Methanol	ns	44.7	60.0	26.1	22.2	17.9
Ethanol	ns	66.7	24.6	15.4	7.2	14.5
1-Butanol	ns	27.2	14.9	7.9	6.7	11.3
Cyclohexanol	ns	20.2	18.4	2.2	5.2	9.8
Ethylene glycol	ns	195	—	9.48×10^3	185	21.2
Propylene glycol	ns	152	—	1.91×40^5	103.2	18.3
1,3-Butanediol	ns	115	—	362	89.7	16.6
Glycerol	ns	208	—	1.42×10^3	1.33×10^4	24.6
Isopropanol	ns	21.8	18.5	19.0	7.0	11.8
Dipropylene glycol	ns	86.5	323	187	—	—
Nitromethane	ns	13.8	15.3	—	5.6	10.2
1-Nitropropane	ns	4.5	1.4	—	3.6	3.6

Note: The solubility radius of PEMA is 10.4.

Table 11. Prediction of PBMA Solubility Using Hansen Solubility Parameters and Group Contribution Models with the Ω_1^∞-Rule of Thumb.

Solvent	s/ns	EFV	UFV	GCF	FVHi	D_{Ha}
Hexane	ns	7.1	7.0	10.7	7.8	8.3
n-Octane	ns	6.7	6.3	11.4	6.7	8.1
n-Decane	ns	6.5	6.1	10.7	6.4	8.1
n-Dodecane	ns	6.6	1.0	16.3	5.9	8.1
n-Hexadecane	ns	6.8	6.1	13.2	5.6	8.1
Toluene	s	3.8	4.4	4.7	4.1	7.1
Xylene	s	2.3	3.6	5.7	3.7	6.3
Methylene dichloride	s	3.3	2.5	3.0	6.1	4.7
Chloroform	s	1.9	9.1	1.7	1.8	4.5
Carbon tetrachloride	s	2.2	7.2	9.9	2.1	8.5
Ethylene dichloride	s	3.5	3.0	—	2.8	4.3
Trichloroethylene	s	2.5	2.9	23.2	2.6	4.9
Chlorobenzene	s	2.5	3.0	6.0	3.4	7.4
o-Dichlorobenzene	s	1.3	2.5	2.7	3.4	7.1
Acetone	s	10.2	14.1	11.1	4.7	5.1
MEK	s	8.4	10.5	6.2	4.3	3.6
MIBK	s	6.3	7.7	5.7	4.2	2.2
Acetophenone	s	8.1	9.3	8.6	6.5	8.3
Ethyl acetate	s	6.7	6.7	5.0	3.7	1.3
Butyl acetate	s	5.5	5.1	4.5	3.8	1.9
Diethyl ether	s	5.2	5.8	11.5	5.6	3.9
THF	s	3.8	4.0	—	4.1	2.8
1,4-Dioxane	s	4.1	4.4	159	4.0	7.4
Methanol	ns	23.7	57.7	35.7	40.0	17.8
Ethanol	ns	29.2	31.3	42.3	13.3	13.9
1-Butanol	ns	18.1	17.1	8.1	11.8	9.9
Cyclohexanol	ns	24.3	70.1	3.0	8.9	8.3
Ethylene glycol	ns	33.1	105	1.59×10^4	512	21.0
Propylene glycol	ns	213	—	1.18×10^3	304	17.8
1,3-Butanediol	ns	959	—	526	289	16.3
Glycerol	ns	295	—	8.88×10^3	6.58×10^4	24.5
Isopropanol	ns	23.7	21.6	10.6	11.6	10.5
Isobutanol	s	99.0	17.9	3.5	10.1	10.1
Diethylene glycol	ns	240	—	2.47×10^3	463	16.2
Dipropylene glycol	ns	128	946	258	—	—
Nitromethane	ns	16.7	14.2	—	9.0	13.3
1-Nitropropane	s	4.7	5.2	—	5.2	7.0
N,*N*-Dimethylformamide	s	3.8	—	—	16.0	10.3

Note: The solubility radius of PBMA is 8.5.

PMMA/ester systems and for systems containing ketones, the results with all three models (EFV, UFV, GCF) are generally wrong. The Hansen solubility-parameter model generally has problems with the PVAc-systems and the systems containing PBMA and alkanes.

Table 13 lists the total number of correct and incorrect answers for all four polymers. Both EFV and FVHi are capable of providing approximately the same number of correct answers as the Hansen solubility-parameter model, but perhaps more interesting is that the number of incorrect answers obtained from EFV is clearly lower than the number obtained from the Hansen solubility-parameter model.

We have also tested the validity of the rule of thumb in systems containing PIBMA, for which no Tait parameters are available. FVHi and the Hansen solubility-parameter model were not tested due to lack of solubility parameters for PIBMA. The results in Table 14 show the same trends, that is, the rule of thumb yields good results for all systems except for those containing ketones.

For some of the alcohols the values of the calculated activity coefficients are very high. These, combined with the rule of thumb, are generally in agreement with the solubility indications [nonsolvent (ns)]. However, those values obtained with GCF for alcohols with two or three hydroxyl groups seem to be unrealistically high. An extension of the GCF parameter table will be required to improve its performance in these and other systems containing “very difficult” (strongly associating) components. Some of these components have already been introduced in the UNIFAC parameter tables, for example, ethylene glycol.

Even though GCF was the best model at infinite dilution, it is the worst model for this application. The rule-of-thumb evaluation includes some extra solvents as compared to the calculations at infinite dilution. Apparently, more problems with the volume calculation in GCF appear for these extra solvents. This explains why GCF performs worse with the rule of thumb than for the infinite dilution calculations.

Clearly, the weakness of the rule of thumb is evident in many cases. The experimental infinite dilution activity coefficient may require extrapolation to the temperature of interest (Holten-Andersen and Eng, 1988). In the 6 to 8 range, the procedure does not provide an answer, and with infinite dilu-

Table 12. Prediction of PVAc Solubility Using Hansen Solubility Parameters and Group Contribution Models with the Ω_1^∞-Rule of Thumb

Solvent	s/ns	EFV	UFV	GCF	FVHi	D_{Ha}
Hexane	ns	38.7	38.6	30.4	8.7	7.1
Toluene	s	2.6	8.0	1.6	4.0	2.3
Chloroform	s	0.1	1.2	1.7	1.8	2.0
Carbon tetrachloride	ns	3.3	4.2	5.3	2.1	4.1
Ethylene dichloride	s	2.7	2.7	—	2.8	6.0
Chlorobenzene	s	3.8	3.7	2.0	3.2	4.0
Acetone	s	5.6	6.8	7.3	4.5	9.7
MEK	s	5.4	6.5	6.3	4.2	7.6
MIBK	ns	6.5	7.8	6.0	4.4	6.0
3-Heptanone	ns	8.5	9.4	6.3	4.1	4.0
Diisobutyl ketone	ns	15.3	10.2	4.4	4.5	3.5
Ethyl acetate	s	4.8	4.8	5.2	3.6	5.7
Butyl acetate	s	6.0	5.8	6.2	3.8	4.5
Diethyl ether	ns	11.4	10.5	16.5	6.0	6.3
THF	s	8.4	5.6	—	3.9	5.6
1,4-Dioxane	s	4.2	3.3	117	3.8	4.4
Methanol	s	18.9	19.4	12.7	34.8	21.5
Ethanol	ns	15.2	38.9	14.3	11.4	17.1
1-Butanol	ns	14.7	11.1	9.2	10.2	12.7
Cyclohexanol	ns	8.4	6.6	—	7.8	9.7
Ethylene glycol	ns	7.4	6.3	5.10×10^3	400	23.7
Diethylene glycol	s	27.8	—	736	340	19.5
Dipropylene glycol	s	27.3	213	123	—	—
Nitromethane	s	3.9	3.8	—	8.0	17.0

Note: The solubility radius of PVAc is 4.1.

Table 13. Validity of Solubility Answers from the Hansen Solubility Parameter Model and Group Contribution Models Used with the Ω_1^∞ Rule of Thumb for Systems Containing PMMA, PEMA, PBMA, and PVAc

Answer	EFV	UFV	GCF	FVHi	Ha
Correct	91	78	72	86	90
Incorrect	19	21	26	23	32
No answer	19	17	14	13	0
No calculation	0	13	17	7	7
Total	129	129	129	129	129

tion activity coefficients outside this range, erroneous results are possible. If a model is available, additional testing by means of the complete concentration-activity diagram is recommended.

We illustrate this with the two systems, acetone/PVAc and carbon tetrachloride/PVAc, for which the activity-concentration diagrams are shown in Figure 2. The infinite dilution activity coefficient of acetone in PVAc calculated from UFV is 6.8, that is, in the range where the rule of thumb is inconclusive. Here, the activity-concentration diagram provides us with the answer (in agreement with the experiment) that acetone is a good solvent for PVAc, as the acetone activity is monotonically increasing.

In contrast, with carbon tetrachloride/PVAc, EFV yields an infinite dilution activity coefficient of 3.3, which deviates only 7% from experimental values (four data points included in the subsection on the results obtained from the group-contribution models). The rule of thumb thus indicates miscibility, in contrast to experimental observations, and also in contrast to the activity-concentration diagram that correctly predicts immiscibility.

We can thus conclude that using the entire activity-concentration diagram is a safer and theoretically more sound method for solvent selection.

Conclusions

Three group-contribution models Entropic FV, UNIFAC FV, and GC-Flory, and four versions of the Flory-Huggins/solubility parameter approach were tested for their capability to predict infinite dilution solvent activity coefficients in paint-related resins. Additionally, it was investigated whether it is possible to use a simple rule of thumb for selecting solvents for paint resins. We summarize here the basic conclusions of our investigations:

- The performance of the group-contribution models is very sensitive to the definition of the molecules in terms of UNIFAC atomic groups. The presumably most correct way of splitting polyacrylate polymers into UNIFAC atomic groups is to use the two new atomic groups CHCOO and CCOO. Their group parameters have been introduced here. Still, empirical UNIFAC group divisions may be equally or even more successful than the new groups.
- We have investigated how the models work for the two commercial epoxy resins, Araldit 488 and Eponol-55, for which the experimental volumes are not available. By using volumes estimated by two different methods, we have shown that, in contrast to Entropic FV, UNIFAC FV is highly sensitive to the volume. Using one of these volume-estimation methods, the solvent activity coefficient calculations compare reasonably well with the experimental data.

Table 14. Prediction of PIBMA Solubility Using Group Contribution Models with the Ω_1^∞-Rule of Thumb

Solvent	s/ns	EFV	UFV	GCF
Hexane	ns	7.2	6.8	8.2
Toluene	s	3.2	4.2	3.6
Xylene	s	2.2	3.5	4.2
Methylene dichloride	s	3.2	2.3	2.9
Chloroform	s	1.9	1.9	2.0
Carbon tetrachloride	s	2.2	2.1	2.6
Ethylene dichloride	s	3.4	2.8	—
Trichloroethylene	s	2.5	2.6	16.0
Chlorobenzene	s	2.4	2.8	2.4
o-Dichlorobenzene	s	1.2	2.4	2.0
Acetone	s	10.6	13.2	8.5
MEK	s	8.1	9.9	6.3
MIBK	s	6.1	7.3	4.5
Acetophenone	s	7.7	8.7	7.0
Ethyl acetate	s	6.5	6.4	3.8
Butyl acetate	s	5.1	4.9	3.4
Diethyl ether	s	5.2	5.5	7.7
THF	s	3.8	3.8	—
1,4-Dioxane	s	4.0	4.2	67.1
Methanol	ns	42.3	53.6	29.0
Ethanol	ns	28.0	33.7	18.9
1-Butanol	ns	17.5	17.7	8.9
Cyclohexanol	ns	22.8	18.5	—
Ethylene glycol	ns	30.3	100	2.72×10^4
Propylene glycol	ns	194	—	3.06×10^3
1,3-Butanediol	ns	145	—	847
Glycerol	ns	269	—	319×10^3
Diethylene glycol	ns	216	—	3.69×10^3
Dipropylene glycol	ns	116	2.13×10^4	398.4
Nitromethane	ns	15.7	15.8	—
1-Nitropropane	s	4.6	4.9	—

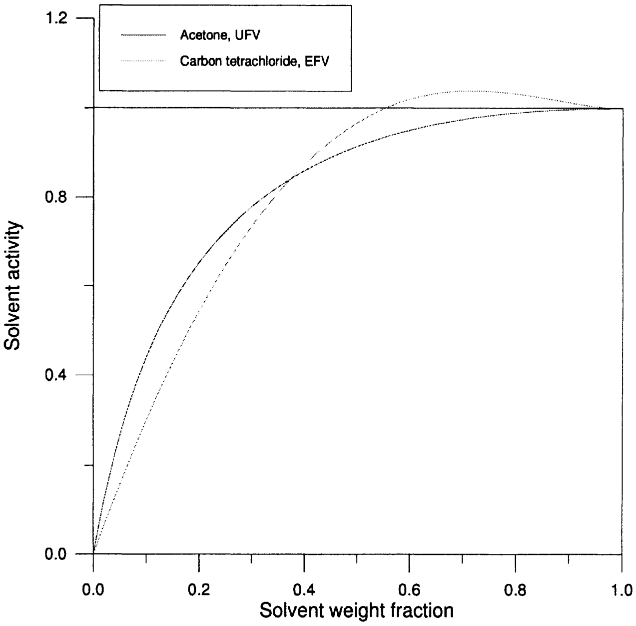

Figure 2. Activity composition for PVAc/acetone obtained from UFV and PVAc/carbon tetrachloride from EFV.

- For all types of systems investigated, the GC-Flory model is the most successful model in the prediction of infinite dilution solvent activity coefficients. GC-Flory does not require the volume as input, and must therefore be considered as a very promising model for systems containing paint resins. However, it has a limited parameter table compared to the UNIFAC methods. This reduces its range of applicability. For those cases where the system contains "difficult" components (such as ethylene glycol), Entropic FV is recommended, since it is less sensitive than UNIFAC FV and more accurate for hydrogen bonding solvents.
- The best of the four Flory-Huggins/solubility-parameter models is the one based on free volume fractions in combination with Hildebrand solubility parameters. The method is comparable to the two activity coefficient models, but is less accurate than GC-Flory, especially for the hydrogen-bonding systems. We further conclude that Hansen solubility parameters do not account only for energetic effects in the systems investigated here. Thus, their use with the Flory-Huggins model in the present versions is not recommended.
- The rule of thumb is in most cases able to point out solvents and nonsolvents for acrylate paint resins. Entropic FV, which is the safest model to use for this application, is comparable to the original Hansen solubility-parameter model.
- In contrast to the rule of thumb, the construction of the entire activity-concentration diagram will always provide an answer as to whether a chemical acts as a solvent or nonsolvent for a resin.

This work is part of an on-going project on the thermodynamics of paints and coatings. Future investigations will focus on improved combinations of the Flory-Huggins and Hansen solubility parameter models, VLE of complex polymer solutions containing hydrogen bonding, aqueous and mixed solvents and on liquid–liquid equilibria of multicomponent polymer solutions.

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Notation

a = activity
D = Hansen solubility distance, $\mathrm{MPa}^{1/2}$
g = molar Gibbs free energy, J/mol
G = Gibbs free energy, J
M = molecular weight, g/mol
N = number of
P = pressure, bar
r = polymer/solvent molar volume ratio
R = ideal gas constant, 8.314 [J/(mol·K)]; radius of solubility sphere in Hansen 3-D plots [$\mathrm{MPa}^{1/2}$]; UNIFAC volume parameter
Q = UNIFAC surface-area parameter
T = temperature, K
V = molar volume, cm^3/mol
$\bar{v}$ = reduced volume
w = weight fraction
x = mol fraction

Greek letters

γ = molar-based activity coefficient
δ = solubility parameter, $\mathrm{MPa}^{1/2}$
θ = θ-temperature, K
ϕ = volume fraction
χ = Flory-Huggins parameter
Ω = weight-based activity coefficient

Subscripts and superscripts

1 = component index for the solvent
2 = component index for the polymer
DP = data points
h = enthalpic; hydrogen bonding
i = component index
m = mixture
p = polar
s = entropic
sys = systems
v = dispersion and polar
comb = combinatorial
d = dispersion
E = excess
FV = free volume
res = residual (energetic)
vdW = Van der Waals
∞ = infinite dilution

Abbreviations

ASOG = analytical solution of groups
comb = combinatorial
EFV = entropic free volume
EoS = equation of state
GCF = group contribution Flory equation of state
GCLF = group contribution lattice fluid
GC-vol = group contribution volume
FH = Flory-Huggins
FV = free volume
FVHa = free volume fractions/Hansen solubility parameters
FVHi = free volume fractions/Hildebrand solubility parameters
Ha = Hansen
Hi = Hildebrand
LCST = lower critical solution temperature
LLE = liquid–liquid equilibrium
MEK = methyl ethyl ketone
MIBK = methyl isobutyl ketone
NRTL = nonrandom two fluid
ns = nonsolvent
VLE = vapor–liquid equilibrium
VOC = volatile organic contents
PBMA = poly(butyl methacrylate)
PDMS = poly(dimethyl siloxane)
PEA = poly(ethyl acrylate)
PEMA = poly(ethyl methacrylate)
PIBMA = poly(isobutyl methacrylate)
PMA = poly(methyl acrylate)
PMMA = poly(methyl methacrylate)
PVAc = poly(vinyl acetate)
PR = Peng-Robinson
PVC = poly(vinyl chloride)
res = residual
s = solvent
SAFT = statistical associated-fluid theory
SRK = Soave-Redlich-Kwong
THF = tetrahydrofurane
UCST = upper critical solution temperature
UFV = UNIFAC-free volume
UNIFAC = universal functional activity coefficient
V = volume
VHa = volume fractions/Hansen solubility parameters
VHi = volume fractions/Hildebrand solubility parameters
vdW = van der Waals

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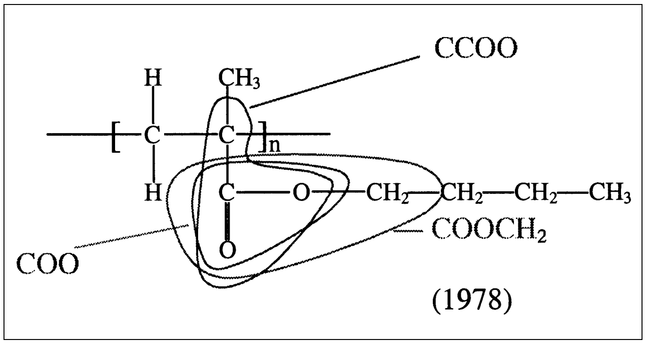

Figure A1. Different ways of splitting PBMA into UNIFAC atomic groups.

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Appendix: Choosing Proper Atomic Groups for Polyacrylates

Standard UNIFAC tables do not contain all group parameters that are necessary when dealing with systems containing polyacrylates and -methacrylates. As an illustration of this, we consider poly(*n*-butyl methacrylate) (PBMA), which has the molecular structure shown in Figure A1.

A "natural" way of splitting the molecule into atomic groups might be to use the CCOO groups, as shown in Figure A1. The problem is that the CCOO group is not present in the UNIFAC table. This topic has also been discussed by Lee and Danner (1997). According to the authors, the COO group should be used. This may be doubtful, since originally the COO group was only meant to be used for benzoates or other compounds where the carbon atom of COO is attached to a group containing π-electrons (Rasmussen, personal communication, 2000). This special atomic group therefore gives rise to interactions with the acetate family functional group (main group). There is no physical justification for this. In the original UNIFAC-FV article, Oishi and Prausnitz (1978) list the CH_2COO group as a $COO{-}CH_2$ group. Apparently, this is wrong.

A more reasonable way to treat PBMA is to introduce CCOO as a new subgroup in the main group of the acetate family, which is assigned volume- and surface-area parameters using the bond lengths given by Bondi (1968). Due to the additivity of the volume and surface parameters, the new parameters can also be calculated from the UNIFAC table. Similarly, we have introduced a CHCOO group, which appears in other polyacrylates, such as poly(methyl acrylate).

Table A1. Subgroups and Their Volume- and Surface-Area Parameters Used in Different Group-Division Methods

Method	Subgroup	R	Q
New	CCOO	1.2215	0.880
New	CHCOO	1.4489	1.108
Prausnitz	CH_2COO	1.6764	1.420
Prausnitz	CH_3COO	1.9031	1.728
Danner-1	COO*	1.3800	1.200
Danner-2	COO**	1.0020	1.200

*Fitted volume- and surface-area parameters.
**Physical volume- and fitted surface-area parameters.

As part of this work we have investigated the effect of the choice of UNIFAC groups for polyacrylates and -methacrylates in the calculation of the solvent activity coefficient at infinite dilution. Table A1 lists the volume- and surface-area parameters for the different subgroups used according to the methods mentioned earlier.

The calculations including the COO group were performed in two different ways, as explained in the following. In the UNIFAC table the COO group appears with fitted volume- and surface-area parameters. This procedure is employed for groups that pose particular problems for UNIFAC. By allowing more parameters to be adjustable, some extra accuracy is achieved. The first set of calculations (Danner-1) was based on these fitted volume- and surface-area parameters.

The nonenergetic contribution to the activity coefficient caused by differences in size, shape, and free volume in the model should not be ruled by adjustable parameters, since they directly influence the free volumes, which are quantities with a physical significance. Hence, the contributions from differences in size, shape, and free volume should be based on the physical volume parameters rather than on the fitted ones.

For the COO group all parameters of the residual contribution to the activity coefficient have been fitted simultaneously, that is, the validity of the group interaction parameters of COO rely on the value of its surface parameters. Therefore, the fitted surface-area parameters of COO should be used in the calculations; the second set of calculations, including the COO group (Danner-2), was based on the physical volume parameters that appear in the FV term and on the fitted surface-area parameters that appear in the residence (energetic) term.

Activity coefficients of solvents at infinite dilution in poly(acrylates) have been calculated based on the different group divisions. The calculation results are shown in Table A2 as their average absolute deviations from experimental values collected from the two databases DIPPR (Danner and High, 1993) and Dechema (Wen et al., 1991). In this comparison we have considered 27 systems with nonpolar solvents (101 data points), 12 systems with polar solvents (35 data points), and 14 systems with solvents capable of forming hydrogen bonds (75 data points).

Table A2. Average Absolute Deviation in %: Experimental vs. Calculated Solvent Activity Coefficients at Infinite Dilution

Type of Solvents	EFV	UFV
New		
Nonpolar	31	29
Polar	18	20
Hydrogen bonding	72	87
Prausnitz		
Nonpolar	25	19
Polar	16	20
Hydrogen bonding	22	36
Danner-1		
Nonpolar	20	57
Polar	26	92
Hydrogen bonding	38	124
Danner-2		
Nonpolar	25	15
Polar	18	23
Hydrogen bonding	26	24

The abbreviations of each of the methods shown in the table will be used in the following discussion.

As can be seen in Table A2, "Prausnitz" yields more accurate results than "New." This holds for all types of systems and for both models. The probability for an arbitrary main group to be positioned next to the ester functional group (resulting in an interaction) is assigned too high a value when the Prausnitz group division method is employed. The fact that this leads to more accurate results indicates that the relevant interaction parameters have been assigned too low numerical values in the UNIFAC tables.

When using the COO group, the EFV gave deviations of several hundred percent for systems containing acetates. The same behavior of EFV was observed by Lee and Danner (1997). In these systems the acetate−COO interaction causes the activity coefficients to attain unrealistically high values. Thus, we believe that an error has been introduced in the estimation of the acetate−COO interaction parameter (which should theoretically be very close to zero). The four systems containing acetates were therefore not included in the average deviation of EFV shown in Table A2.

For nonpolar systems, "Danner-1" and Danner-2" yield similar results for EFV but not for UFV. In the other cases, significantly better results are obtained with Danner-2 than with Danner-1 (very pronounced with UFV). This confirms that it is more appropriate to use the physical volume parameters in the computation of the nonenergetic contributions to the activity coefficient.

The Danner-2 results are better than the New results and of approximately the same accuracy as the Prausnitz results.

From the preceding results we can conclude that both using the CH_2COO and CH_3COO groups (Prausnitz) and using the COO group with physical volume parameters (Danner-2) in systems containing polyacrylates and -methacrylates yield better results than when using the CCOO and CHCOO groups introduced here (New). Still, the latter assignment of UNIFAC groups is possibly the physically more correct one. In practical applications, calculated activity coefficients may not always be checked against experimental values, and the physically most correct way of splitting the molecules into UNIFAC groups should be chosen. Therefore, for the polyacrylates and -methacrylates, we have based the calculations in this article on the new UNIFAC groups.

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