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A Model-based Solvent Selection and Design Framework for Organic Coating Formulations

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ABSTRACT

Selection of solvents and calculation of their composition in the final product, is a critical step in coating formulation design. This task can be facilitated by computer-aided methods if the necessary thermodynamic and group contribution property models along with chemical property data are available for the ingredients under consideration. However, these computer-aided procedures must be supplemented and verified by using experimental procedures. Hence, the computer-aided stage can be used to speed-up the solvent selection and design process, efficiently utilize experimental resources and serve as a guide for the formulation chemist.

We present in this work an adaption of the generic Computer-Aided Product Design (CAPD) methodology for organic coating formulations. Herein, the paper discusses a model-based framework developed for the design of solvents for such coatings. The applicability of this framework is tested via a case study wherein, solvents for the dispersion of two specific organic pigments are required to be determined, when acrylic polymers are used as dispersing aids.

KEYWORDS: Solvent Design, Organic Coatings, Chemical Property Data, Thermodynamic Models, Computer-Aided Algorithms

1. Introduction

Coatings have a broad range of application in different industrial sectors ranging from marine to domestic where they serve two main purposes: to protect a surface from mechanical, chemical or biological damage when it comes in contact with the surrounding media; and to decorate a surface by adding color or luster and smooth out any irregularities on the surface. The term ‘coating’ encompasses a number of materials like enamels, lacquers, varnishes, undercoats, surfacers, primers, sealers, fillers, stoppers and many others¹. However, these are all formulated on the same basic principles and contain some or all of the four basic ingredients: colorant, binder, liquid and additive².

Depending on the application area of the coating, the particle phase may comprise pigments having varied functionalities like imparting colour, resisting corrosion, conducting electricity and heat; or simply used as extenders for hiding, stain blocking and increased scrub resistance³.

While formulating a coating, often the desirable behavior of the final product is known. Accordingly, it is required to determine the identity of the constituents, which when combined in appropriate amounts, will deliver the desired properties and hence the performance. A typical approach for formulating new coatings involves seeking the guidance of raw material suppliers and experienced formulators. As per their recommendation, a coating formulation chemist chooses the appropriate raw materials to develop the formulation that meets the required specifications. Then, an attempt to formulate a sample experimentally in the laboratory, is made. Usually, the composition needs to be modified multiple times until the target specifications are achieved⁴.

Alternatively, such a formulation design problem can be solved using an integrated experiment-modeling approach⁵. In this approach, predictive models with a wide application range are used to screen candidate ingredients for the product formulation via computer-aided tools. The formulation ingredients and composition obtained from this screening stage are further evaluated using rigorous models or experimental procedures. Making use of this approach, can significantly reduce the resources and time taken to design a formulation when compared to the typical trial-and-error based experimental approach⁶.

To further improve the efficiency of the integrated experiment-modeling approach, the Design of Experiments (DoE) method can enable the formulator to further decrease the number of experiments, while maintaining the same level of accuracy of the design.

Specifically, in the case of organic solvent-based decorative coating formulations, the pigment and the binder perform the main function of decorating by conferring a particular colour and are hence

the active ingredients of the formulation. Due to a large number of solvents available to disperse the pigment and solubilize the binder, the selection of an optimum solvent mixture for formulating a liquid coating can be challenging. Moreover, the coatings industry is the single largest user of organic solvents and as much as one third of the total raw material cost is that of solvents⁷. The organic solvent evaporation, that occurs after the application of coatings, contributes significantly to the Volatile Organic Compounds (VOCs) emissions to the atmosphere⁸. Therefore, the amount of solvent used must be optimized, such that, both the cost and environmental impact are minimal. A low environmental impact here implies that the environmental properties like aquatic toxicity and bioaccumulation factor should have a low value while biodegradation potential should have a high value⁹. A model-based methodology using computer-aided tools can help to systematize the design and selection of these solvents.

For the computer-aided design of solvent-based formulations, Conte et al.¹⁰ proposed a workflow, which comprises four steps: define the needs of the product formulation, identify the active ingredient, select solvents for the active ingredient and finally correct the formulation properties using additives. However, this workflow is a part of a generic formulation design framework and does not discuss the details of the specific needs and properties for a coating formulation. Besides, the conversion of the qualitative needs to target properties that can be quantified, requires a systematic approach. For instance, it is challenging to find a suitable quantifiable target property corresponding to the need of a 200 μm coating film to protect a particular substrate for 10 years under normal atmospheric conditions.

Therefore, the aim of this work is to comprehensively expand and adapt the third step on ‘selection of solvents for the active ingredient’, in order to design a liquid organic coating formulation.

2. Methodology and Associated Modeling Tools

2.1 Scope of the Developed Framework

A framework for solvent design and selection for organic coating formulations with a liquid delivery system is developed. This comprises a methodology workflow, the corresponding methods and tools for solvent design as well as the information required to be supplied by the user at each step (Figure 1). The framework developed in this work however cannot be used for water-based formulations and formulations containing inorganic pigments.

The methodology developed in this work comprises seven steps: problem definition for solvent design, single molecular solvent design, binary solvent mixture design, solvent-polymer compatibility check and solvent-polymer-pigment compatibility check, verification of designed solvents, final solvent selection based on optimization objective. It is illustrated in Figure 1 and all steps are discussed hereafter.

Figure 1: Framework for Computer-Aided Solvent Design for Coating Formulations

2.2 Algorithms, Model Library and Databases

To aid this methodology, a set of algorithms, a comprehensive model library and databases are used. These are either available or implemented via tools (computer programs).

2.2.1 Algorithms

On one hand, the computer-aided molecular design (CAMD) algorithm developed in the work by Gani et al.¹¹ designs single molecular organic solvents that satisfy the specified structural and property constraints. On the other hand, the mixture design algorithm (MIXD) developed in the work by Conte et al.¹² yields thermodynamically stable binary solvent mixtures that satisfy the specified target property constraints. The CAMD and MIXD algorithms are available via the ProCAMD tool of ICAS 21¹³ and the ProCAPD tool¹⁴ respectively. The scientific basis of these algorithms is available in the Supporting Information.

2.2.2 Model Library

The model library, available via the ProPred and ProCAMD tools of ICAS 21¹³, consists of pure component property prediction models for organic compounds as well as polymers. They are based on a group contribution approach. The UNIFAC activity coefficient models for estimation of mixture properties, are also available via this library. The linear mixing rules, for the property prediction for mixtures with negligible excess properties, can be used via the ProCAPD tool¹⁴. On the other hand, the non-linear models are used only for verification of mixtures with significant excess properties, after the screening stage is completed. These are not directly available via any of the above-mentioned tools.

2.2.3 Knowledge base and Database Library

A ‘knowledge base’, consisting of a guide for the translation of performance criteria or needs of the final formulation to quantifiable target properties, is developed using literature, patents and consumer

surveys (Table S2.1 of the Supporting Information). Besides, it also contains information and typical properties of industrial solvents (Table S2.2 of the Supporting Information), as well as, regulatory limits amassed using official documents from the regulatory bodies like the REACH regulations from European Chemical Agency (Table S2.3 of the Supporting Information). These are taken as reference to set the constraint values on target properties. However, the user can also decide to improve the constraint values, in order to improve the existing design of the product.

Apart from the ‘knowledge base’, various property databases constitute the ‘database library’. A ‘solvents database’ includes several pure component properties of the solvents that are commonly used in paint formulations and are compiled in the work by Conte et al.¹² In this work, this property database is expanded to include the ‘Hansen Solubility Parameters (HSP)’ of these solvents (Table S3 of the Supporting Information). Additionally, polymer and pigment databases containing their HSP and ‘radius of solubility ($R_{o,pol}$)’, are developed. These are available in the Tables S5 and S6 of the Supporting Information respectively.

2.3 Steps in the Model-based Solvent Design Methodology

2.3.1 Problem Definition for Solvent Design

Depending on the desired solvent-related attributes and needs in the final coating formulation, the target properties of the solvent, which can be quantified, are recognized. These target properties could be ‘physicochemical’ and ‘environmental, health and safety (EH&S)’ and ‘phase-equilibria’-related properties. The constraints on these properties are selected using the ‘knowledge base’ as explained in Section 2.2.3. Most importantly, the ‘Active Ingredients’ (AIs), which are the polymer and pigment in case of a coating, should be dissolved and dispersed respectively by the solvent. Accordingly, for the dissolution of the polymer, the assumption by Hancock et al.¹⁵ is used to set the constraints on the total HSP of the solvent (or solvent mixture), δ_{sol} .

$$\delta_{pol} - 3 \leq \delta_{sol} \leq \delta_{pol} + 3 \quad (1)$$

δ_{pol} is the total HSP of the polymer in MPa^{1/2}

It may not be possible to directly translate some of the needs to physicochemical properties, even though they may affect the design choices made later. For instance, the compatibility of the solvent with the surface of application for the coating cannot be translated to target properties considered in the scope of this framework.

2.3.2 Single Molecular Solvent Design

Using the molecular building blocks of the compounds that cover the range of solvents used in the coatings industrial sector, single molecular solvents are designed with the ProCAMD tool in ICAS 21¹³. This tool generates all feasible structures using a set of structural rules¹⁶ and screens them using group-contribution models based on the Marrero and Gani (MG-GC⁺¹⁷) method, such that they satisfy the constraints specified in 2.2.1.

2.3.3 Binary Solvent Mixture Design

One or more solvent databases, consisting of names of the solvents and their pure component properties, is selected from the ‘database library’ corresponding to the requirements of the coating. For instance, for the design of a waterproof coating, the selection of a ‘water insoluble solvents’ database is appropriate. Next, the MIXD algorithm is used to design the solvent mixtures wherein the property models to calculate the pure component properties (incase the experimental value is not available) and the mixture properties as well as activity coefficient models to determine the mixture stability are used. The optimum composition corresponding to the lowest cost of the designed mixture and the mixtures properties are obtained as an output.

2.3.4 Solvent (or Solvent Mixture) and Polymer Compatibility Check

The compatibility of the designed single molecular solvents and binary solvent mixtures is checked by calculating the RED_{pol} of the polymer - solvent system, which is the ratio of the ‘Hansen solubility distance between the polymer and the solvent, $R_{a,pol}$ ’ to the ‘radius of solubility of the polymer’, $R_{o,pol}$. A RED_{pol} value of less than one indicates solubilization of the polymer in the solvent (Eq. 2). However, in order to avoid pigment flocculation and sedimentation, a RED_{pol} value close to 1 indicating marginal solvency is preferred for pigmented coatings¹⁸.

$$RED_{pol} = \frac{R_{a,pol}}{R_{o,pol}} = \frac{\sqrt{4(\delta_{d,pol}-\delta_{d,sol})^2 + (\delta_{p,pol}-\delta_{p,sol})^2 + (\delta_{h,pol}-\delta_{h,sol})^2}}{R_{o,pol}} < 1 \quad (2)$$

Moreover, due to the introduction of the polymer into the solvent mixture, other target properties like viscosity and surface tension of the polymer solution will change. The polymer solution viscosity ($\eta_{pol,solution}$) can be estimated using the following equation given by T.C. Patton¹⁹,

$$\eta_{pol,solution} = \eta_{sol,298K} 10^{\left(\frac{W}{k_a - k_b W}\right)} \quad (3)$$

where, W is the weight fraction of the polymer while $k_{a,b}$ are constants. Here, it is assumed that the polymer is nonvolatile. To evaluate the two constants, the solution viscosities at two different polymer weight fractions must be known.

2.3.5 Solvent (or Solvent Mixture), Polymer and Pigment Interactions Effect

Similar to Step 2.2.4, the HSP of the pigment ($\delta_{d,pig}$, $\delta_{p,pig}$, $\delta_{h,pig}$) can be retrieved from the ‘pigment property database’ and the RED_{pig} can be estimated using Eq. 4. The RED_{pig} value is required to be greater than one, denoting that the solvent mixture is a poor solvent for the pigment particles and hence will facilitate the dispersion of the pigment particles.

$$RED_{pig} = \frac{R_{a,pig}}{R_{o,pig}} = \frac{\sqrt{4(\delta_{d,pig}-\delta_{d,sol})^2 + (\delta_{p,pig}-\delta_{p,sol})^2 + (\delta_{h,pig}-\delta_{h,sol})^2}}{R_{o,pig}} > 1 \quad (4)$$

A 3-dimensional plot consisting of the HSP of the pigment, polymer and the solvent as well as the solubility sphere of the pigment and polymer is constructed to visualise the solubility interactions between these three components.

Additionally, according to Schröder, the total HSP of the pigment ($\delta_{HSP,pig}$) calculated using

$\sqrt{\delta_{d,pig}^2 + \delta_{p,pig}^2 + \delta_{h,pig}^2}$ must lie in between the total HSP of the polymer and the solvent²⁰. This

ensures that the composite vehicle (solvent + polymer) has an HSP value close to that of the pigment and hence the polymer adsorption on the surface of the pigment is optimum²¹.

Moreover, the particle size and shape of the pigment have a significant effect on the viscosity of the formulation. Additionally, if we have additives in the formulation, they must be activated during the production in order to deliver a similar viscosity.

2.3.6 Verification of the Designed Solvents

The designed solvents (or solvent mixture) are verified using experimentally tested formulations that are reported either in patents or open source literature or simply by performing experiments in the laboratory.

2.3.7 Final Selection of Solvent Based on the Optimization Objective Function

Finally, the solvent corresponding to the optimum value of the objective function is selected. The optimization objective could either be to minimize the cost or the environmental impact. Apart from performing a single objective optimization, a multi-objective optimization may also be performed, for instance to arrive at a solution that is both environmentally friendly and cost effective. However, the most optimum solution may not always be the best solution for the system, given the uncertainties in the models used and the fact that the models are based on certain assumptions and do not include the effects due to interactions. Therefore, it is useful to have all robust solutions that satisfy the target property constraints range ordered in the decreasing order of the optimization objective value.

3. Case-Study

The applicability of the developed framework is tested using a pigment dispersion case-study.

3.1 Problem Description

It is known that the ‘Malvern Panalytical Mastersizer’ is used for the measurement of particle size distribution by means of the laser diffraction technology²². One of its applications is in the coatings industrial sector wherein it can be used to measure the particle size of pigments.

The Mastersizer has a ‘Wet Dispersion Unit’. In this unit, the pigment particles are dispersed in an aqueous or organic solution, before they are pumped into the measurement cell. But wetting of the pigment particles with deionized water or solvent alone is not sufficient to yield a stable solution. (For the stability, it is necessary to keep the pigment particles apart). A polymer that anchors to the pigment particles and is also soluble in the solvent can disperse and stabilize the pigment particles by steric stabilization²³ in solvent borne coatings. On the other hand, a surfactant could be used to stabilize the pigment in an aqueous solution by the electrostatic or ionic stabilization mechanism²⁴. However, the addition of the polymer or surfactant should be such that flocculation and sedimentation of the pigment particles do not occur.

Therefore, it is desired to determine the solvent or solvent mixture along with the polymeric resin and/or surfactant that is compatible with a given pigment particle to allow for a well-distributed dispersion using a model-based methodology. Here it is to be noted that this would be equivalent to reconstituting a basic coating formulation.

3.2 Methodology Implementation and Results

The model-based methodology is implemented by following the steps below.

3.2.1 Problem Definition for Solvent Design

Two organic pigments, ‘Heliogen® Blue 6930L BASF’ and ‘Palietol® Yellow L1820 BASF’ are considered for the dispersion. Further, to aid the dispersion process, two acrylic polymers, Poly(methyl methacrylate) (PMMA) and Poly(ethyl methacrylate) (PEMA) that can provide steric stabilization to the dispersion, are considered. This generates four combinations of pigment and polymer. The objective of the problem is to design a solvent or solvent mixture, for each of these four combinations.

The qualitative needs for the solvent design are translated to target properties, which can be quantified. The constraints on these target properties are selected as shown in Table 1.

The total HSP for the polymers ($\delta_{HSP,pol}$), PMMA and PEMA are $22.28 \text{ MPa}^{1/2}$ ($\delta_{d,pol} = 18.8 \text{ MPa}^{1/2}$, $\delta_{p,pol} = 10.5 \text{ MPa}^{1/2}$ and $\delta_{h,pol} = 5.7 \text{ MPa}^{1/2}$) and $19.82 \text{ MPa}^{1/2}$ ($\delta_{d,pol} = 17.9 \text{ MPa}^{1/2}$, $\delta_{p,pol} = 7.8 \text{ MPa}^{1/2}$ and $\delta_{h,pol} = 3.4 \text{ MPa}^{1/2}$) respectively. These are used to set the constraints on the total HSP of the solvent according to the condition mentioned in Section 2.2.1.

Table 1: Constraints on Target Properties

User Needs	Target properties	Target property constraints	Reference for Target Constraint Selection
Solubilize Polymer	total hansen solubility parameter of solvent ($\delta_{HSP,sol}$)	$\delta_{HSP,pol} - 3 < \delta_{HSP,sol} (\text{MPa}^{1/2}) < \delta_{HSP,pol} + 3$	Polymer Solubility Condition given by Hancock et al. ¹⁵
Easily Flowable	dynamic viscosity (η_{298K})	$0.6 < \eta_{sol,298K} (\text{cP}) < 0.9$	Industrial Solvents
Adequate Wetting	molar volume ($V_{m,298K}$), surface tension (σ_{298K})	$100 < V_{m,298K} (\text{l.kmol}^{-1}) < 130$ $26.5 < \sigma_{298K} (\text{mN.m}^{-1}) < 29.5$	Material and Safety Data Sheets ^{25–28}
Good Stability (for solvent mixtures)	Gibbs energy of mixing (ΔG_{mix}), tangent plane distance (TPD)	$\Delta G_{mix} / RT < 0$ TPD > 0	Thermodynamic Stability Conditions ^{29–31}

The constraints on the surface tension (σ_{298K}), molar volume ($V_{m,298K}$) and dynamic viscosity ($\eta_{sol,298K}$) are chosen using the ‘knowledge base’. Herein, typical industrial solvent properties are used to set the constraints on these target properties of the solvents required to be designed. In the case of design of binary mixtures of solvents, it is also desired that there is no phase separation. Therefore, accordingly the conditions on Gibbs energy of mixing (ΔG_{mix}) and tangent plane distance (TPD) are chosen.

3.2.2 Single Molecular Solvent Design

The molecular building blocks to design acyclic alkanes, alcohols, esters, ethers, aldehydes, ketones, chlorine containing compounds and aromatic hydrocarbons are chosen. 14307 acyclic and 38 aromatic structures are generated using these blocks, wherein the maximum number of same functional groups in a molecule is limited to six. 14 compounds out of these 14345 feasible structures satisfy the constraints specified on $\eta_{sol,298K}$, $V_{m,298K}$ and σ_{298K} in Table 1. This molecule generation and screening is carried out in the ProCAMD tool in ICAS 21¹³. All these 14 compounds (Table 2) also satisfy the constraints on $\delta_{HSP,sol}$ when PEMA is used as the polymer, while only the first 6 compounds satisfy the constraints on $\delta_{HSP,sol}$ when PMMA is used as the polymer. The screening for each property is shown schematically in Figure 2.

Table 2: Single Molecular Solvents Satisfying the Specified Constraints when PEMA is the Selected Polymer

Groups	Name	$\eta_{sol,298K}$ (cP)	$V_{m,298K}$ (l/kmol)	σ_{298K} (mN/m)	$\delta_{HSP,sol}$ (MPa ^{1/2})
Acyclic Solvents					
2 CH ₂ + 1 CHO + 1 CH ₂ Cl	4-chlorobutanal	0.80	97.57	27.45	21.62
1 CH ₂ + 1 CH ₃ CO + 1 CH ₂ Cl (+CH ₃ COCH ₂ second order)	1-chloro-3-butanone	0.82	98.80	28.89	20.04
2 CH ₂ + 2 CH ₂ Cl	1,4-dichloro butane	0.66	112.29	29.25	19.86
1 CH ₃ + 1 CHCl + 1 CHCl ₂	1,1,2-Trichloropropane	0.89	111.18	27.85	19.70
1 CH ₃ + 1 CH + 2 CH ₂ Cl	1,3-dichloro 2-methyl propane	0.65	111.96	26.67	19.56

1 CH ₂ + 1 CH ₃ COO + 1 CH ₂ Cl	2-chloroethyl acetate	0.82	105.30	28.65	19.52
1 CH ₃ + 1 CH ₂ Cl + 1 COO	Methyl chloroacetate	0.65	95.21	26.51	18.66
1 CH ₃ + 1 CH ₂ CO + 1 CH ₂ Cl	1-chloro-2-butanone	0.82	100.57	28.38	18.85
1 CH ₃ + 1 CH ₂ O + 1 CHCl ₂	1,1-dichloro-2-ethoxymethane	0.60	107.78	27.73	18.77
1 CH ₂ + 1 CH ₃ O + 1 CHCl ₂	1,1-dichloro-2-methoxyethane	0.60	105.64	27.81	18.79
1 CH ₃ + 1 CH ₂ + 1 CH ₂ Cl + 1 COO	ethyl 2-chloroacetate	0.82	111.73	26.73	18.52
2 CH ₂ + 1 CH ₃ O + 1 CHCl ₂	1,1-dichloro-3-methoxypropane	0.75	122.15	28.03	18.68
2 CH ₃ + 1 CHCl + 1 COO	methyl 2-chloro propanoate	0.82	112.00	27.23	17.47
Aromatic Solvents					
1 CH ₃ + 5 ACH + 1 ACCH ₂	ethyl benzene	0.63	122.48	27.14	18.36

Figure 2a.

Figure 2b

Figure 2: Single Molecular Solvents Screening based on Specified Target Property Constraints considering Two Selected Acrylic Polymers a) PEMA b) PMMA

Although the designed single molecular solvents satisfy the specified physicochemical property constraints, they are known to have EH&S-related hazards ($-\log LC_{50} > 3.3$ ($\log \text{mol.L}^{-1}$); $BOD_5 / COD < 0.5$, $-\log LD_{50} > 1.5$)^{32,33}. Hence, they are not a good choice for solvent candidates from the EH&S perspective.

Therefore, apart from the single molecular solvents, the suitability of binary solvent mixtures for the given problem is explored in the next step.

3.2.3 Binary Solvent Mixture Design

Starting from a ‘solvent database for paint formulations’, available via the ‘database library’, 465 binary solvent mixtures are evaluated using the MixD algorithm, available via the ProCAPD tool. The algorithm provides estimates of the properties, $\eta_{sol,298K}$, $V_{m,298K}$ and σ_{298K} of these mixtures, using linear mixing rule while the stability of the mixture is determined using the UNIFAC³⁴ activity coefficient model with LLE group contributions³⁵ to predict ΔG_{mix} and TPD . 42 mixtures satisfy the constraints on these properties. These mixtures along with their optimized composition (x₁) corresponding to the lowest price of the mixture, are obtained as an output from the algorithm (Table S4 of the Supporting Information). 39 mixtures among the 42 mixtures designed above, also satisfy the constraints on $\delta_{HSP,sol}$ which is calculated using the linear mixing rule, when PEMA is selected as a polymer (Table 3). However, only the first five mixtures of Table 3 satisfy the constraints on $\delta_{HSP,sol}$, when PMMA is selected as a polymer.

Table 3: Binary Solvent Mixtures Satisfying the Specified Constraints when PEMA is the Selected Polymer

Mixture No.	Solvent 1		Solvent 2	x_I (Composition corresponding to Minimized Cost) (mol/ mol)	$\eta_{sol,298K}$ (cP)	$V_{m,298K}$ (l/kmol)	σ_{298K} (mN/m)	$\delta_{HSP,sol}$ (MPa ^{1/2})
1	2-ethyl hexanol	+	2-Propanol, 1-propoxy-	0.112	0.9	101.1	29.186	21.67
2	ethylene glycol monopropyl ether	+	2-Propanol, 1-propoxy-	0.379	0.9	103.626	29.2	22.22
3	2-Propanol, 1-propoxy-	+	Ethanol, 2-butoxy-	0.698	0.9	107.55	29.431	21.56
4	2-Propanol, 1-propoxy-	+	Ethanol, 2-butoxy-, acetate	0.685	0.6	120.414	28.88	20.66
5	Methane, dichloro-	+	Ethanol, 2-butoxy-, acetate	0.668	0.609	100	27.375	19.46
6	2-Butanol	+	methylbenzene	0.016	0.6	106.919	28.405	18.16
7	2-Butanol	+	Benzene, ethyl-	0.1	0.9	119.773	27.724	17.84
8	1-Propanol, 2-methyl-	+	methylbenzene	0.015	0.6	106.951	28.411	18.15
9	1-Propanol, 2-methyl-	+	Benzene, ethyl-	0.094	0.9	120.074	27.763	17.80
10	1-Butanol	+	methylbenzene	0.02	0.6	106.856	28.428	18.16
11	1-Butanol	+	Benzene, ethyl-	0.127	0.9	118.941	27.872	17.91
12	2-ethyl hexanol	+	Benzene, ethyl-	0.043	0.9	123.329	28.262	17.83
13	ethylene glycol monopropyl ether	+	methylbenzene	0.028	0.6	107.364	28.51	18.17
14	Ethanol, 2-butoxy-	+	methylbenzene	0.021	0.6	107.682	28.521	18.15
15	Ethanol, 2-butoxy-	+	Benzene, ethyl-	0.134	0.9	124.08	28.457	17.83
16	Ethanol, 2-(2-ethoxyethoxy)-	+	methylbenzene	0.013	0.6	107.473	28.535	18.16
17	Ethanol, 2-(2-butoxyethoxy)-	+	methylbenzene	0.008	0.6	107.664	28.532	18.16
18	Ethanol, 2-(2-butoxyethoxy)-	+	methylbenzene	0.003	0.6	107.494	28.523	18.16
19	methylbenzene	+	Benzene, ethyl-	0.53	0.6	114.53	28.406	18.02
20	methylbenzene	+	xylene	0.791	0.6	110.626	28.552	18.10
21	methylbenzene	+	Acetic acid, butyl ester	0.676	0.6	115.471	27.327	17.75
22	methylbenzene	+	Acetic acid, hexyl ester	0.906	0.6	112.671	28.264	18.02
23	methylbenzene	+	butyrolactone	0.959	0.6	106.774	28.66	18.29
24	methylbenzene	+	Cyclohexanone	0.971	0.6	107.074	28.675	18.18
25	methylbenzene	+	2-Pentanone, 4-hydroxy-4-methyl-	0.995	0.6	107.252	28.5	18.16
26	methylbenzene	+	Ethanol, 2-butoxy-, acetate	0.955	0.6	110.034	28.465	18.09
27	methylbenzene	+	Ethanol, 2-(2-butoxyethoxy)-, acetate	0.985	0.6	108.666	28.533	18.15
28	Benzene, ethyl-	+	hexane	0.867	0.6	123.721	26.994	17.46
29	Benzene, ethyl-	+	heptane	0.825	0.601	126.75	26.5	17.41
30	Benzene, ethyl-	+	Acetic acid ethyl ester	0.785	0.6	117.615	27.246	17.64
31	Benzene, ethyl-	+	Acetic acid, butyl ester	0.474	0.668	128.09	26.5	17.36
32	Benzene, ethyl-	+	Acetic acid, hexyl ester	1	0.647	122.856	28.3	17.87
33	Benzene, ethyl-	+	2-Butanone	0.813	0.6	116.767	27.607	17.72
34	Benzene, ethyl-	+	Methane, dichloro-	0.901	0.6	117.073	28.191	17.97
35	xylene	+	hexane	0.78	0.656	124.971	26.5	17.19
36	xylene	+	heptane	1	0.758	123.741	28.75	17.90
37	Acetic acid ethyl ester	+	Cyclohexanone	0.722	0.865	100.044	26.5	18.50
38	Acetic acid, butyl ester	+	butyrolactone	0.784	0.878	125.247	26.5	18.89
39	Acetic acid, hexyl ester	+	Methane, dichloro-	0.517	0.6	116.743	26.58	18.55

*The stability criterion of $\Delta G^{mix}/RT$ is fulfilled for all the mixtures mentioned in the table

3.2.4 Solvent (or Solvent Mixture) and Polymer Compatibility Check

Next, the compatibility of the designed single molecular solvents (Table 2) and the binary solvent mixtures (Table 3) with the polymer is checked using the ‘Hansen solubility sphere’ calculations. In order to avoid pigment flocculation and sedimentation a RED_{pol} value close to 1 indicating marginal solvency is preferred. Only four solvent mixtures (Table 4), when either PMMA or PEMA is used as polymer, satisfy this condition.

Table 4: Binary solvent mixtures with RED_{pol} close to 1

No.	Mixture	x_1	RED_{PMMA}	RED_{PEMA}
1	2-ethyl hexanol (1) + 2-propanol, 1-propoxy (2)	0.11	1.24	1.04
2	ethylene glycol monopropyl ether (1) + 2-propanol, 1-propoxy (2)	0.38	1.19	1.04
3	2-Propanol, 1-propoxy- (1) + Ethanol, 2-butoxy-, (2)	0.70	1.22	1.02
4	2-Propanol, 1-propoxy- (1) + Ethanol, 2-butoxy-, acetate (2)	0.69	1.17	0.95

The change in viscosity and surface tension due to the introduction of the polymer has not been considered here.

3.2.5 Solvent (or Solvent Mixture), Polymer and Pigment Interactions Effect

Finally, the compatibility of the pigment required to-be dispersed is checked with the vehicle (solvent mixture and polymer). The $\delta_{HSP,pig}$ and $R_{o,pig}$ for ‘Heliogen® Blue 6930L BASF’ are $18.87 \text{ MPa}^{1/2}$ ($\delta_{d,pig}= 18 \text{ MPa}^{1/2}$, $\delta_{p,pig}= 4 \text{ MPa}^{1/2}$, $\delta_{h,pig}= 4 \text{ MPa}^{1/2}$) and $4 \text{ MPa}^{1/2}$ respectively, while that of ‘Paliotol® Yellow L1820 BASF’ are $21.9 \text{ MPa}^{1/2}$ ($\delta_{d,pig}= 18.9 \text{ MPa}^{1/2}$, $\delta_{p,pig}= 3.5 \text{ MPa}^{1/2}$, $\delta_{h,pig}= 10.5 \text{ MPa}^{1/2}$) and $5.4 \text{ MPa}^{1/2}$ respectively. These are retrieved from the ‘pigment database’ in the ‘database library’. The RED_{pig} calculated for the four solvent mixtures obtained in the previous step considering each of the two organic pigments considered in this problem, is estimated (Table 5). It is seen that, all four solvent mixtures satisfy the condition, ‘ $RED_{pig} > 1$ ’.

This implies that the solvents are outside the solubility radius of the pigment and are good for the dispersion process.

Table 5: RED_{pig} for Binary Solvent Mixtures

No.	Mixture		x_1	$RED_{Heliogen®Blue}$	$RED_{Paliotol®Yellow}$
1	2-ethyl hexanol (1)	+ 2-propanol, 1-propoxy (2)	0.11	2.72	1.45
2	ethylene glycol monopropyl ether (1)	+ 2-propanol, 1-propoxy (2)	0.38	2.80	1.51
3	2-Propanol, 1-propoxy- (1)	+ Ethanol, 2-butoxy-, (2)	0.70	2.65	1.40
4	2-Propanol, 1-propoxy- (1)	+ Ethanol, 2-butoxy-, acetate (2)	0.69	2.45	1.39

A 3-dimensional plot of HSP and their projections on the 2D-planes is constructed. This helps to view the positioning of HSP of the four designed solvent mixtures ($\delta_{d,sol}$, $\delta_{p,sol}$, $\delta_{h,sol}$) and study their affinity with the solubility spheres, for all four combinations of pigments and polymers. These plots are shown in Figure 3: 3-Dimensional Plot for the Hansen Solubility Parameters and Solubility Spheres of Heliogen® Blue Pigment and a) PMMA Polymer b) PEMA Polymer Figure 3 and 4 for the dispersion of ‘Heliogen® Blue 6930L BASF’ pigment and the ‘Paliotol® Yellow L 1820 BASF’ pigment respectively.

The change in viscosity and surface tension due to the introduction of the pigment, has not been considered here.

3.2.6 Verification of Designed Solvent Mixtures

The solvent candidates designed as a result of the above steps, are either a mixture of ‘alcohols and alkoxyated alcohols’ or ‘alkoxyated alcohols and glycol ethers’. These classes of organic compounds are used in the formulation of acrylic lacquers for automotive refinish³⁶. Besides, aromatics such as toluene and xylenes are also versatile solvents for industrial acrylic coatings³⁷. Therefore, the results obtained from the computer-aided stage are suitable for the dispersion of the organic pigments using the chosen acrylic polymers.

The high molecular weight alcohols ensure that they are not miscible with water and hence will not take up water from the atmosphere. They also aid in control of viscosity during application of the paint³⁸. Most importantly, oxygenated solvents are environmentally friendly.

3.2.7 Final Selection of Solvent Based on the Optimization Objective Function

Lastly, the verified solvent mixtures are ranked on the basis of cost. The solvent mixture with the lowest price is ‘2-Propanol, 1-propoxy- and Ethanol, 2-butoxy-’ and costs 487 \$/kmol (or 4.2 \$/kg). Correlations used to calculate the cost are those that are developed in the work of Conte et al.¹² The pricing data to develop these correlations is obtained from ICIS price reports³⁹. The cost of the optimum binary solvent mixture is higher compared to the currently used aromatic solvents like methyl benzene (1.1 \$/kg) and ethyl benzene (3.9 \$/kg). However, as described in the previous section, it has a lower environmental impact.

Figure 3: 3-Dimensional Plot for the Hansen Solubility Parameters and Solubility Spheres of Heliogen® Blue Pigment and
a) PMMA Polymer b) PEMA Polymer

Figure 4: 3-Dimensional Plot for the Hansen Solubility Parameters and Solubility Spheres of Paliotol® Yellow Pigment and
a) PMMA Polymer b) PEMA Polymer

The $\delta_{HSP,pig}$ of ‘Heliogen® Blue 6930L BASF’ does not lie in between the $\delta_{HSP,sol}$ of any of the four solvent mixtures and the $\delta_{HSP,pol}$ of either of the two polymers. However, in the case of ‘Paliotol® Yellow L1820 BASF’, the condition ‘ $\delta_{HSP,sol} < \delta_{HSP,pig} < \delta_{HSP,pol}$ ’, is satisfied for the solvent mixtures ‘1’, ‘3’ and ‘4’ when PMMA is used as the polymer. Also, the condition ‘ $\delta_{HSP,sol} > \delta_{HSP,pig} > \delta_{HSP,pol}$ ’ is satisfied in the case of solvent mixture ‘2’ when PEMA is used as the polymer. This ensures that the acrylic polymer adsorption on the pigment surface will be optimum when these four solvent mixtures are used in the case of the yellow pigment.

3.3 Sensitivity Analysis

A sensitivity analysis is performed in order to assess the effect of the choice of constraints (or boundaries) on the design and selection of the solvent (or solvent mixture) for dispersion case-study. This analysis is carried out for both the pigments in the case when PEMA is selected as the polymer.

The original boundaries on the target properties (Table 1) are relaxed and constrained individually by 2% and 5%. The values of the new boundaries corresponding to each attempt of relaxing or constraining the original boundaries are available in Table S7 of the Supporting Information. As a result of relaxing and constraining the original boundaries on all the target properties simultaneously, the change in the number of suitable solvents for solubilization of the PEMA polymer is recorded and shown in Figure 5.

Figure 5: Effect of Change in the Original Constraints by 2 - 5 % on the Number of Solvent Candidates for the Dispersion of the Two Selected Organic Pigments when PEMA is Used as the Polymer

In the case when the constraints are relaxed by 5%, 17 acyclic and 3 aromatic single molecular solvents as well as 30 binary solvent mixtures are found to have satisfactory properties (Table S8 of the Supporting Information), in addition to those identified using the original constraints shown in Table 2 and 3 .

However, only eight binary mixtures out of the 104 designed solvent candidates (single molecular and binary) also satisfy the conditions on RED for the PEMA polymer and the ‘Paliotol® Yellow L1820 BASF’ pigment, along with satisfying the condition ‘ $\delta_{HSP,sol} > \delta_{HSP,pig} > \delta_{HSP,pol}$ ’. The calculated RED for these binary mixtures is shown in Table 6.

Table 6: Eight Binary Solvent Mixtures that Satisfy All Conditions on Relaxing the Property Constraints by 5%

Solvent 1	Solvent 2	x_I	RED _{PEMA}	RED _{Heliogen}	RED _{Paliotal}
2-Butanol	2-Propanol, 1-propoxy-	0.25	1.08	2.81	1.49
1-Propanol, 2-methyl-	2-Propanol, 1-propoxy-	0.24	1.12	2.92	1.56
1-Butanol	2-Propanol, 1-propoxy-	0.31	1.11	2.89	1.49
2-Propanol, 1-propoxy-	Ethanol, 2-(2-butoxyethoxy)-	0.93	1.04	2.75	1.49
2-Propanol, 1-propoxy-	butyrolactone	0.72	0.86	2.55	1.48
2-Propanol, 1-propoxy-	Cyclohexanone	0.79	0.87	2.31	1.26
2-Propanol, 1-propoxy-	Ethanol, 2-butoxy-, acetate	0.71	0.95	2.47	1.40
2-Propanol, 1-propoxy-	Ethanol, 2-(2-butoxyethoxy)-, acetate	0.88	1.00	2.63	1.43
Benzene, ethyl-	Acetic acid, butyl ester	0.09	1.22	2.93	1.37
Acetic acid, butyl ester	butyrolactone	0.96	1.29	3.16	1.50
Acetic acid, butyl ester	Ethanol, 2-butoxy-, acetate	0.89	1.27	3.09	1.49

Therefore, apart from the four binary mixtures obtained using the original constraints (Table 4Table 3), it may be relevant to experimentally evaluate these eight binary mixtures for the dispersion of the ‘Paliotal® Yellow L1820 BASF’ organic pigment.

4. Conclusion and Perspectives

A systematic model-based methodology has been developed for the design and selection of solvents for organic coating formulations. The applicability of this methodology has been tested via a case-study on dispersion of pigment particles. Four solvent mixtures are recognized as candidates to disperse the ‘Paliotol® Yellow L1820 BASF’ pigment when either PMMA or PEMA are used as polymers. As a result of a sensitivity analysis, eight additional solvent mixture candidates are recognized in the case where the original constraints are relaxed by 5% and PEMA is selected as the polymer. Therefore, this methodology enables a formulation chemist to arrive to a list of reliable solvent mixtures. These can then be verified with experiments, in order to account for all effects in a real mixture.

The scope of using the computer-aided design algorithms is limited by the availability, reliability and accuracy of the models employed to predict the target properties. Due to the lack of availability of property prediction models for water, water-based formulations cannot be designed using the developed framework. As the application range of the methodology depends on the availability and applicability of the property models, the methodology can be expanded by developing and incorporating new models. Once, the required model parameters are estimated and the accuracy, ease of use, predictive capabilities of a developed model is evaluated, it can be easily added to the ‘Model Library’.

Current and future work consists of tackling the design and selection of solvents for other types of coatings, for instance, those that dry by oxidative reactions or by reaction with other ingredients (e.g. polyesters with isocyanates in polyurethane based coatings). Moreover, in the case wherein steric stabilization provided by the polymer is not sufficient for the dispersion of the pigment, one would need to make use of dispersing agents that can provide electrostatic stabilization. In order to do so, additional constraints and conditions are required to be taken

into account during the computer-aided solvent design stage. Besides, the substrate-dependent properties like adhesion strength and anti-wear performance also require an extensive study.

ASSOCIATED CONTENT

Supporting Information

Key scientific methods used in the development of the methodology; results from Task 5 for the case studies applying the developed methodology

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