REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* Jan 2014	**2. REPORT TYPE** Briefing Charts	**3. DATES COVERED** *(From - To)* Jan 2014- Mar 2014

4. TITLE AND SUBTITLE Use of Hansen Solubility Parameters in Fuel Treatment Processes	**5a. CONTRACT NUMBER** In-House **5b. GRANT NUMBER** **5c. PROGRAM ELEMENT NUMBER**
6. AUTHOR(S) Andrew J. Guenthner, Josiah T. Reams, Shawn P. J. Kirby, Arun K. Kota, Gibum Kwon, Anish Tuteja, and Joseph Mabry	**5d. PROJECT NUMBER** **5e. TASK NUMBER** **5f. WORK UNIT NUMBER** Q0BG
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680	**8. PERFORMING ORGANIZATION REPORT NO.**
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive Edwards AFB CA 93524-7048	**10. SPONSOR/MONITOR'S ACRONYM(S)** **11. SPONSOR/MONITOR'S REPORT NUMBER(S)** **AFRL-RQ-ED-VG-2014-046**

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A: Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
Briefing Charts presented at ACS National Meeting and Expo, Dallas, TX., March 16, 2014. PA#14118

14. ABSTRACT
Briefing Charts

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Joseph Mabry
a. REPORT **Unclassified**	**b. ABSTRACT** **Unclassified**	**c. THIS PAGE** **Unclassified**	SAR	17	**19b. TELEPHONE NO** *(include area code)* 661-275-5857

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

USE OF HANSEN SOLUBILITY PARAMETERS IN FUEL TREATMENT PROCESSES

17 March 2014

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Outline

- Background / Motivation
  - Relevant Fuel Treatment Needs
  - Hansen Solubility Parameters
- Dyes
  - Experimental HSP Determination
  - Extrapolation to Other Dyes
- Predictions for Extraction Fluids
  - Quantitative Prediction
  - Sensitivity to Uncertainties
  - Qualitative Predictions
  - Experimental Validation

Acknowledgements: Air Force Office of Scientific Research, Air Force Research Laboratory – Program Support; PWG team members (AFRL/RQRP)

AFRL Mission

Leading the discovery, development, and integration of affordable warfighting technologies for our air, space, and cyberspace force.

Considerations for Rocket Fuel

- Reduced supply-chain logistics
- Decreased risk of supply interruption

Availability

- Reduced coking
- I_{sp} improvement
- Improved thermal stability

Performance

- Reduced logistics cost
- Less Expensive feed

Cost

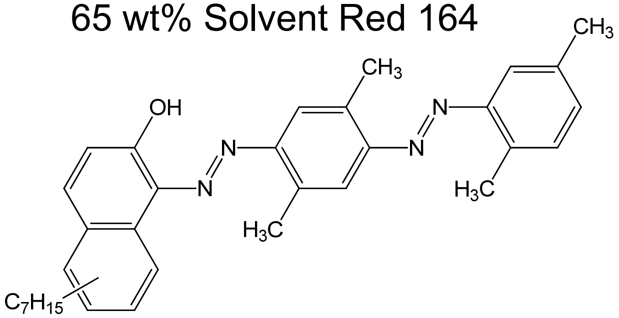
Objective: Utilize liquid/liquid extraction process to improve performance, increase availability, and reduce cost of RP by producing these fuels from less expensive feed streams.

Undesirables in RP-1

Oil Red B4 (ORB4)

Dye in RP-1

65 wt% Solvent Red 164



15-30 wt% xylene

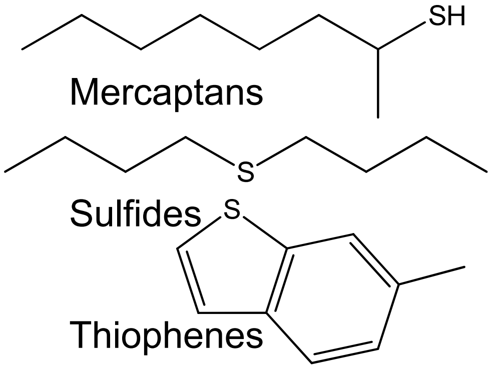
5-10 wt% ethylbenzene

Detrimental to Thermal Stability!

Sulfur Compounds

Present in RP-1

Concentration varies

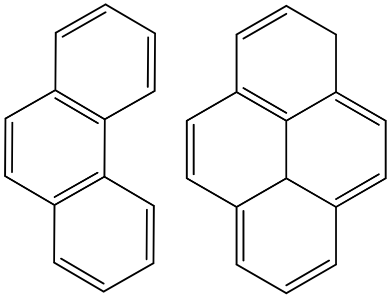


Catalysts for Coking Reactions

Aromatics

Present in RP-1

Concentration varies

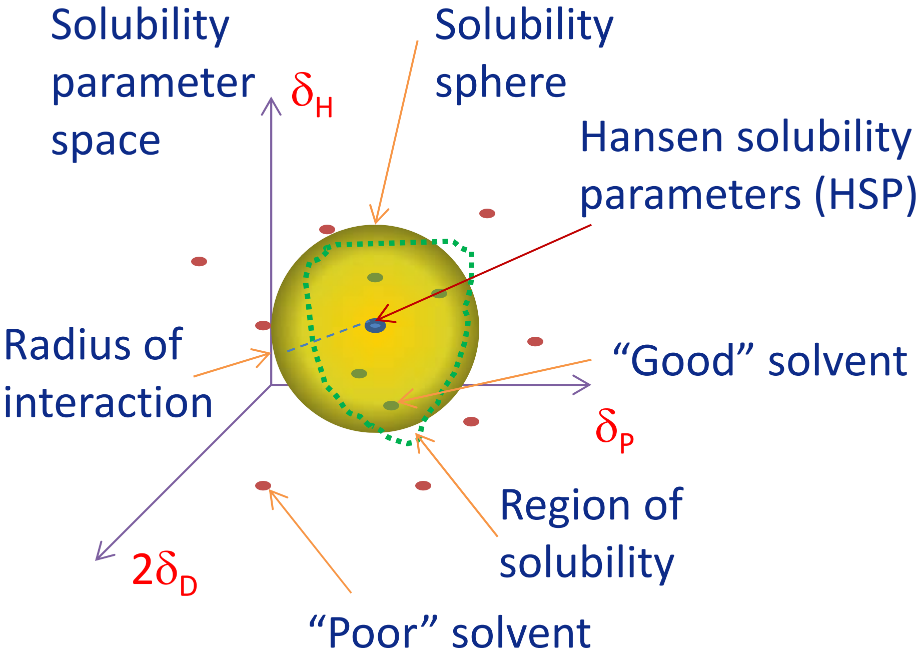


Detrimental to Performance

RP-2 is expensive and requires an additional supply chain, which also consumes resources and may be put at risk due to unforeseen circumstances.

Removal from less expensive feed streams will increase availability, reduce supply risk, reduce cost, and improve performance.

Hansen Solubility Parameters



Solubility parameter space

Solubility sphere

Hansen solubility parameters (HSP)

Radius of interaction

"Good" solvent

Region of solubility

"Poor" solvent

δ_H

δ_P

$2\delta_D$

The traditional approach to estimating Hansen solubility parameters requires trials of typically 30 or 50 different solvents, but is straightforward to carry out. "Good" typically is indicated by >5% or 10% solubility, or by swelling, ESC, etc.

Experimental method for determining HSP

1. Determine solubility (or affinity) in a large set of trial solvents
2. Plot the HSP of "good" and "poor" solvents in a "solubility parameter space" as shown.
3. "Good" solvents normally lie near one another in a "region of solubility"
4. When $2\delta_D$ is used as an axis, the region of solubility is typically bounded by a sphere.
5. The center coordinates of the sphere mark the newly determined HSP.
6. With knowledge of the HSP and "radius of interaction" (test dependent), test results for any subsequent solvent (or mixture) are reliably predicted.

Source: Hansen Solubility Parameters: A User's Handbook, 2nd ed., CRC Press, 2007

Thermodynamic Relations

Solubility parameter

Molar enthalpy of vaporization

Dispersive, polar, and H-bonding components

Enthalpy of mixing

Molar volume

$\delta^2 = (\Delta H_{vap} - RT) / V$

$\delta^2 = \delta_D^{\,2} + \delta_P^{\,2} + \delta_H^{\,2}$

$\Delta H_{mix} = \phi_1 \phi_2 V_{ref}[(\delta_{D1} - \delta_{D2})^2 + (1/4)(\delta_{P1} - \delta_{P2})^2 + (1/4)(\delta_{H1} - \delta_{H2})^2]$

Volume fractions

$K = C_{0,2} / C_{O,1}$

Partition coefficient

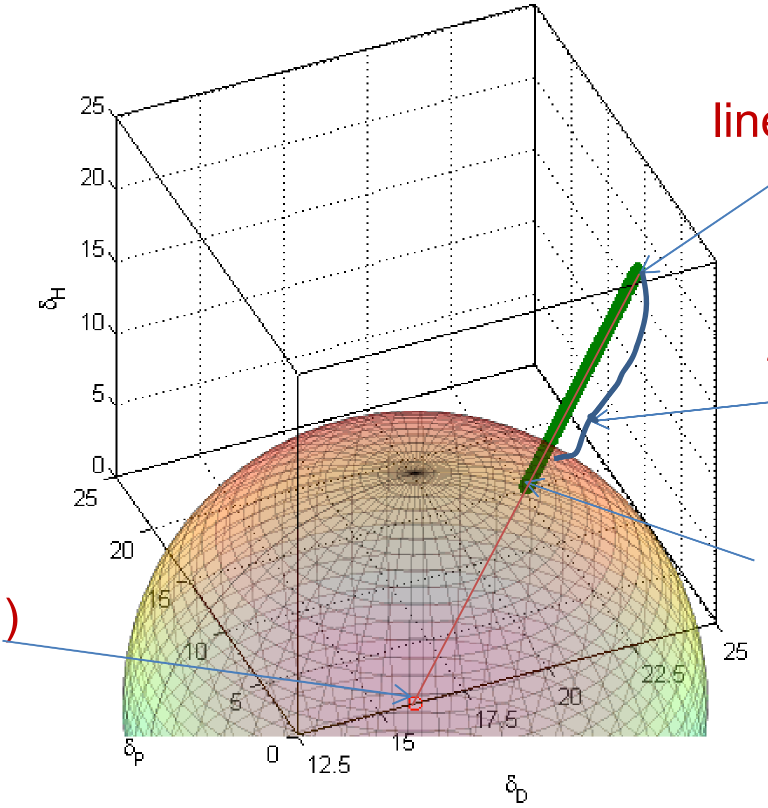
$RT \ln K = V_0[(\delta_{D1} - \delta_{D0})^2 + (1/4)(\delta_{P1} - \delta_{P0})^2 + (1/4)(\delta_{H1} - \delta_{H0})^2 - (\delta_{D2} - \delta_{D0})^2 - (1/4)(\delta_{P2} - \delta_{P0})^2 - (1/4)(\delta_{H2} - \delta_{H0})^2] + RT \ln (V_1/V_2)$

$RT \ln K = V_0(D_{1\text{-}0}^{\,2} - D_{2\text{-}0}^{\,2}) + RT \ln (V_1/V_2)$

$D_{i\text{-}0}$ is the distance in "solubility parameter space" between liquid i and impurity 0. For reference, phase 1 = fuel, phase 2 = extraction fluid.

$D_{i\text{-}0}$ is fixed, so to maximize K, minimize $D_{2\text{-}0}$ subject to constraint that 1 and 2 are not miscible (i.e. maximize $D_{1\text{-}2}$).

Determination of Optimal Extraction Fluid (Graphical)



line connecting 1 and 0

2* (optimal extractants)

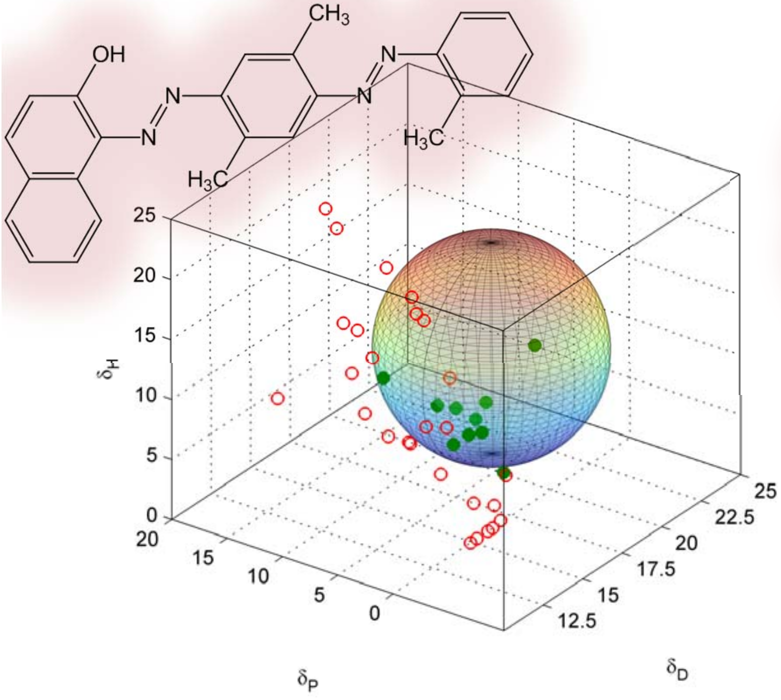
0
(impurity)

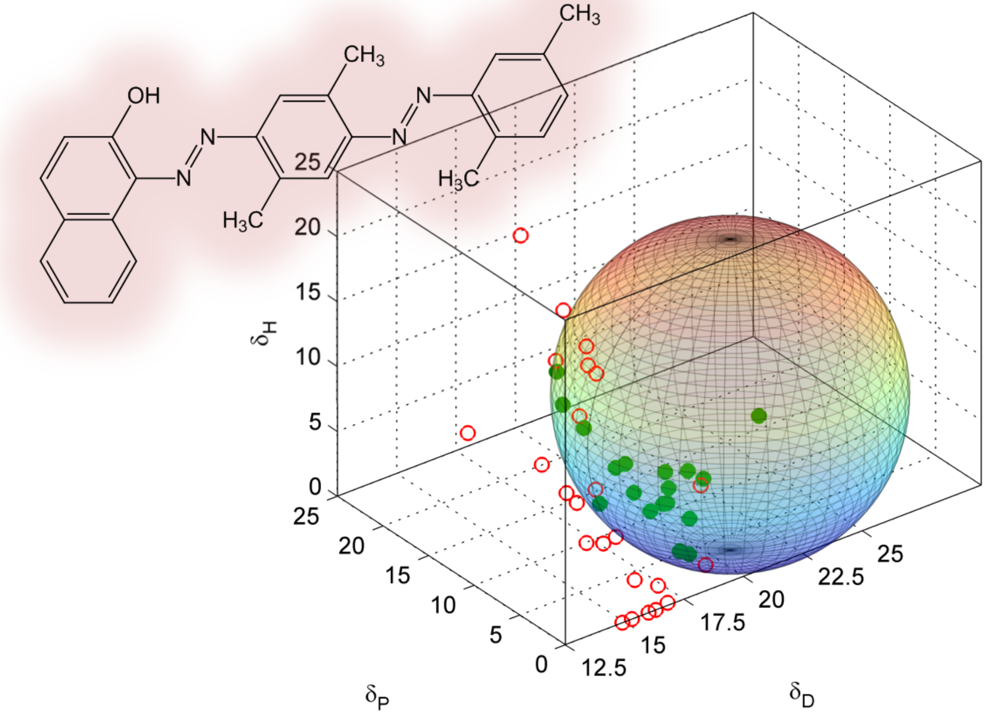
1 (fuel)

Knowledge of HSP of impurity and fuel allows for rational design of optimal extraction fluid based on HSP based on simple geometry.

Optimal fluid will lie along the line connecting points 1 and 0 in HSP space, but outside the sphere of solubility for 1.

HSP Of Oil Red Dyes





Oil Red EGN

$\delta_D = 20.7\ (J/cc)^{1/2}$

$\delta_p = 6.2\ (J/cc)^{1/2}$

$\delta_H = 9.4\ (J/cc)^{1/2}$

Oil Red O

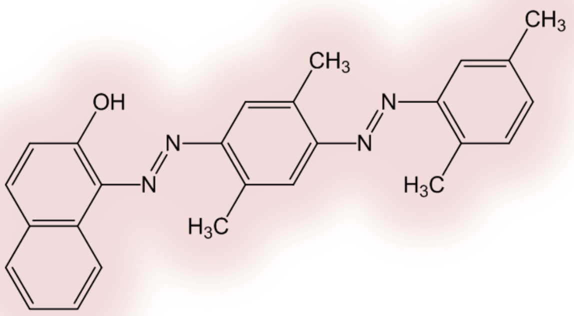
$\delta_D = 21.8\ (J/cc)^{1/2}$

$\delta_p = 5.9\ (J/cc)^{1/2}$

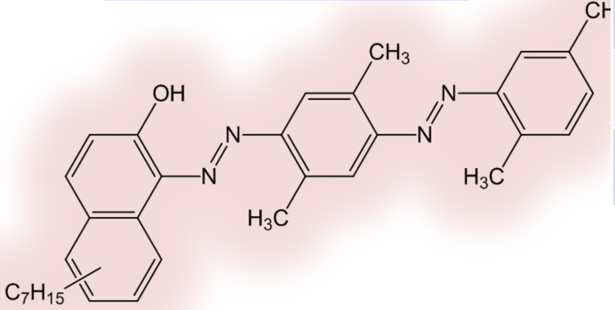
$\delta_H = 10.2\ (J/cc)^{1/2}$

These values are preliminary. The high value of the dispersion parameter may make the sphere-fitting an ill-posed problem.

Computed HSP for Oil Red B4



Oil Red O



Oil Red B4 (solid ingredient)

Oil Red B4 (solids) = Oil Red O + ½ (tetradecane)

	Oil Red O	Heptyl Group	Total
δ_D	21.8	16.2	20.4
δ_P	5.9	0	5.0
δ_H	10.2	0	8.7
V_m (cc/mol)	349	131	480
E_D (J/mol)	166000	34000	200000
E_P (J/mol)	12000	0	12000
E_H (J/mol)	36000	0	36000

Use
$E_i = V_m * \delta_i{}^2$
E_i and V_m values are additive

Good extraction fluids for ORB4 will have a high dispersion parameter!

Quantitative Predictions: Oil Red B4 in Dodecane / IPA:Water 9:1 (vol)

Case #	Scenario	δ_{D1}	δ_{D1}	δ_{D1}	δ_{D1}	δ_{D1}	δ_{D1}	$D_{1\text{-}0}^2$	$D_{2\text{-}0}^2$	K
1	Baseline	16	0	0	15.8	7.1	16.4	178	148	1000
2	Miscibility	16	1.4	3.7	15.8	7.1	16.4	115	148	0.005
3	Water HSP	16	0	0	15.8	7.1	17.4	178	165	40
4	Dye HSP*	16	0	0	15.8	7.1	16.4	217	189	700

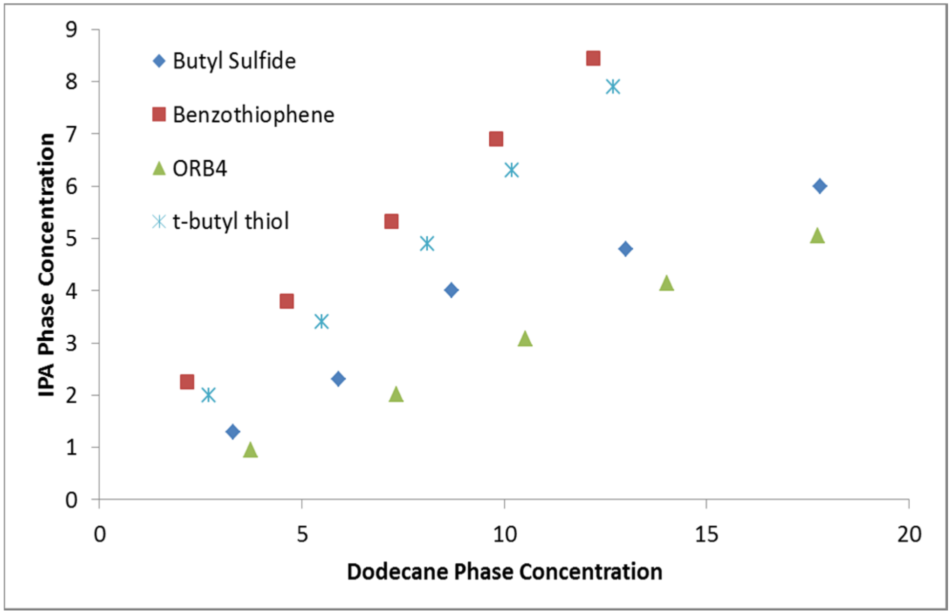
Baseline case assumes no miscibility of dodecane in IPA. Miscibility (case 2) estimates HSP for ~5 vol% IPA in dodecane, based on experience with RP-1.

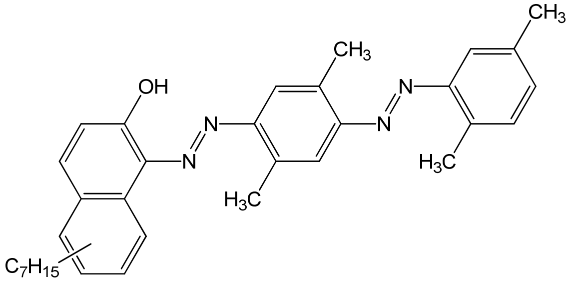
*HSP for Oil Red B4 are $\delta_D = 20.4\ (J/cc)^{1/2}$ $\delta_p = 5.0\ (J/cc)^{1/2}$ $\delta_H = 8.7\ (J/cc)^{1/2}$ for cases 1, 2, and 3. For case 4, $\delta_D = 21.4 (J/cc)^{1/2}$ $\delta_p = 5.0\ (J/cc)^{1/2}$ $\delta_H = 8.7\ (J/cc)^{1/2}$

HSP for IPA : water mixture is estimated based on either apparent values from miscible solvent / water mixtures (cases 1, 2, and 4) and a slightly higher value based on uncertainty in δ_H for water in mixtures (case 3).

Proper assessment of uncertainties , in particular even slight mutual miscibility, is critical for quantitative predictions of K

Extraction Parameter Determination





Experimental data shows K < 1 for a wide variety of RP-1 contaminants extracted in IPA : Water (10:1 by weight)

Optimum IPA : Water ratio is ~13 : 1 based on small scale extractions.

Qualitative Guidance from HSP

- The key feature of many undesirables in RP-1 such as ORB4 (and likely benzothiophene) is a high value of δ_D in comparison to that of mainly aliphatic fuels. This difference is apparent from studies of Hansen Solubility Parameters but not from other heuristic considerations such as “contaminants are more polar” (though Hansen Solubility Parameter studies confirm the higher polarity as well).

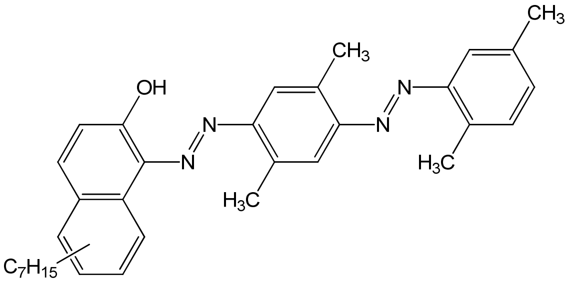
- An optimal extraction medium thus would combine a high dispersive parameter with moderate to high polarity and hydrogen bonding character.

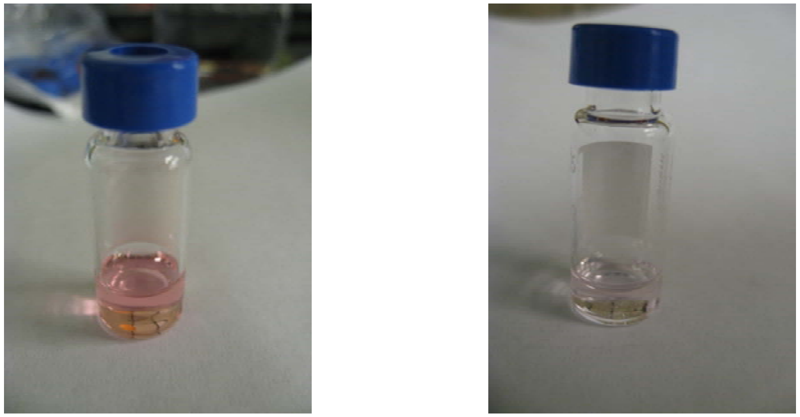
- High values of the dispersion parameter need not require aromaticity. They can, for instance, be achieved through the use of heavy atoms such as bromine or iodine in extraction fluids.

- As an example, a mixture of 80 parts by volume 1,1,2,2-tetrabromoethane and 20 parts by volume dimethylformamide has δ_D = 21.7 (J/cc)$^{1/2}$ δ_p = 7.7 (J/cc)$^{1/2}$ δ_H = 8.9 (J/cc)$^{1/2}$ and shows little or no miscibility towards dodecane. In the purely immiscible “baseline” case, the predicted value for $K > 10^{14}$. Even for 10 vol% miscibility in dodecane and a simultaneous least favorable error of 1 (J/cc)$^{1/2}$ in all three parameters for the dye, K is still about 2000.

Experimental Validation

ORB4 Dodecane before (left) and after (right) contact with IPA : water (10:1 vol.)



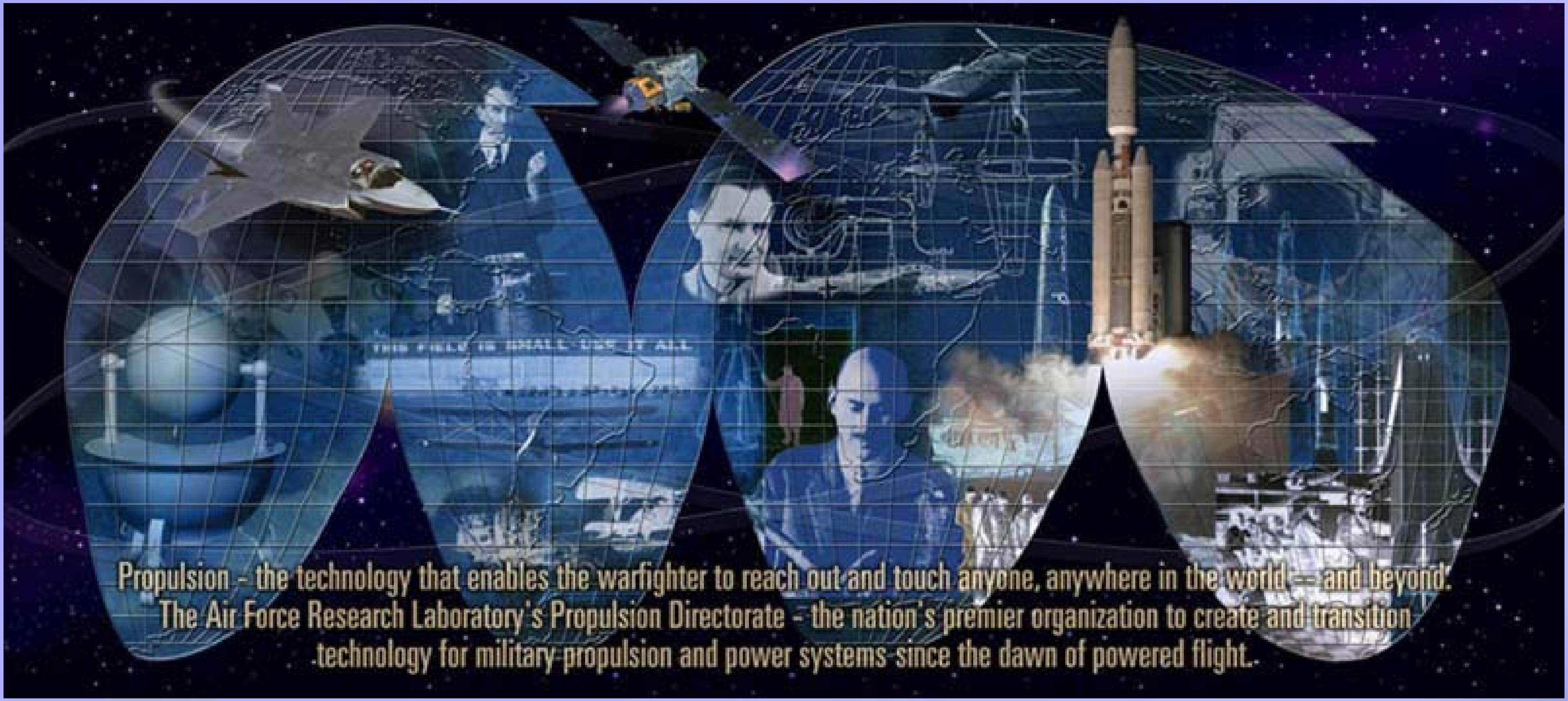


Dodecane before (left) and after (right) contact with 1,1,2,2-tetrabromoethane : dimethylformamide (4:1 vol.)

Images show only one phase. Removal of the dye is much more apparent when the extraction fluid with a high dispersion parameter is used.

Summary / Future Work

- Hansen Solubility Parameters developed for polymers can play a highly useful role in the design of extractive systems for removal of contaminants from high-performance fuel supplies.
  - Hansen Solubility Parameters have been measured for two related Oil Red dyes. The values showed good consistency given the similarity of dye chemical structures, with likely errors of less than about 1 $(J/cc)^{1/2}$ in parameter values.
  - Consistent values enable meaningful estimation of Hansen Solubility Parameters for other closely related dyes where measurement may not be as practical, such as for Oil Red B4.
  - Prediction of partition coefficients from Hansen Solubility Parameters, and the rational design of optimal extraction fluids, is theoretically straightforward and appears robust toward the likely errors in measured Hansen Solubility Parameter values for contaminants and extraction fluids that do not contain water. The predicted vales are highly sensitive to even slight miscibility of the two liquid phases. Nonetheless, qualitative approaches appear to have reliable predictive power.
- Areas for future work include validation with additional extraction fluids and HSP determination for sulfur-containing compounds (which are often too soluble to work with traditional methods of determination)



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