The Choice of Solvents for Cleaning Metal Optics in Order to Increase the Threshold of Optical Damage

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Abstract. Metal optics is actively used in IR optics, which makes it necessary to clean it from dust and other operational contaminants. This increases the life of these notably expensive products. Usually their mechanical wiping is excluded, since it leads to the appearance of scratches and other defects on the surface, markedly increasing the scattering of radiation. Methods for the selection of solvents have been analyzed and experiments have been carried out that make it possible to accept efficient their use in the purification of metal optics from contaminations. Contaminations have different physicochemical properties and are present, as a rule, together on the surface of metal optics (taking into account the corrosion properties of the latter). Solvent compositions based on azeotropes with freon-114B2, having a solubility parameter (δ) corresponding or close to the solubility parameter (δ) of the main (by weight) contamination or a mixture of contaminants which are present on the optical surface, were used.

1. Introduction
Metal mirrors are widely used in IR optics. During operation of metal mirrors, they must be regularly cleaned from dust and other operational contaminants. Particular attention in this case should be applied to cleaning the mirrors of high-power lasers [1].

The group of compounds which are presently used as solvents covers > 300 compounds, without taking into account a virtually unlimited number of solvent mixtures. The differences in their physicochemical properties are large. Already for these reasons it is difficult to classify and select solvents for the purposes of chemical cleaning of metal optics. Taking into account the corrosion properties of metal optics, especially those made from aluminum, copper and their alloys, it is advisable to use dehydrated solvents and their mixtures in the cleaning process. The latter are characterized by a variety of properties associated with different types of intra- and intermolecular interactions, which determine many of their intra- and intermolecular properties. In particular, the role of association processes, specific solvation and formation of complexes is important.

Usually solvents are classified according to the classes of chemical compounds - alcohols, ketones, carboxylic acids, esters, nitrogen-containing compounds, etc. But this approach does not allow one to understand their similarities and differences when choosing the solvents for the purification of various contaminants whose solubility and miscibility in different solvents reflect individual features in the
nature of the interaction between particles in a given system. Therefore, solvents are often classified based on other physical and chemical properties.

In the model of electrostatic solvation [3–5], the effect of constant dipole moment (D) and dielectric constant (μ) for the classification and selection of solvents is highlighted. The dipole-dipole interaction between constant fields is observed, and what is more the magnitude of the dipole of the molecule depends primarily on the size of the molecule and the nature of the functional group present in the molecule (table 1 [2]).

Table 1. Dipole moments of some basic functional groups, K • m. (Kulon meter).

| Group               | μ•10⁻³0 | Group               | μ•10⁻³0 | Group               | μ•10⁻³0 |
|---------------------|---------|---------------------|---------|---------------------|---------|
| -N-- (tertiary amine)| 2.7     | -NH₂- (primary amine)| 4.7     | -NO₂                | 10.7    |
| NH- (secondary amine)| 3.7     | -SOO- (complex ester)| 6.0     | -C                  | 11.7    |
| -O- (simple ether)  | 4.6     | -CO (ketone)        |         |                     |         |

This model treats the ion as a homogeneous conducting ball and the solvent as a continuous medium characterized by a macroscopic dielectric constant (dielectric continuum) and makes it possible to estimate the ion solvation, understood as the difference between the works required charging the model sphere in a vacuum and in a given solvent. In the case of a continuum [3, 6], having a dielectric constant D < 0, this work (W) can be expressed as follows

\[ W = \frac{1}{D} \int_0^\infty q^2 \left( \frac{\partial r}{\partial q} \right)^2 \frac{1}{r^2} \frac{1}{2DR} \left( \frac{2e^2}{2} \right), \]  

where R - is the radius of the ions.

Hence, for the case of thermodynamic solvation [7] of one mole of ions, the change in Gibbs energy (ΔGᵢ) is

\[ \Delta G_i = \left( 1 - \frac{1}{D} \right) N \zeta^2 e^2 / 2R, \]  

and the heat of solvation (ΔHᵢ)

\[ \Delta H_i = \Delta G_i - T \left( \frac{\partial \Delta G_i}{\partial T} \right)_p = \left[ 1 - \frac{1}{D} \left \frac{\partial D}{\partial D} \right \right] N \zeta^2 e^2 / 2R. \]  

However, D is not constant and depends on the electric field strength, and, therefore, on the distance "molecule-ion", the concentration of ions in solution, the structure of solvent molecules, etc. This can be taken into account using the theory of the dielectric nonlinear effect [8], which predicts changes in D of a solvent in the direct vicinity of an ion (E ≈ 10⁻⁹ V / cm²) using the formula

\[ D_d = D - n^2 / 1 + bE^2 + n^2, \]  

where D₅₀ D - dielectric constant differential and at zero field strength (pure solvent), respectively; n is the refractive index of light for pure solvent; b is a constant equal to 1.08 • 10⁻⁸ units. SGS².

The introduction of the expression (4) into the theory of Born's solvation gives the best interpretation [9] of the energy of the processes in formula (2) for the Gibbs energy (ΔGᵢ) of ion solvation.

A complicated version of the electrostatic theory of solvation is possible, where the latter has consistent stages: 1) the formation of the coordination sphere of an ion in the gas phase by the interaction of ions with solvent molecules; 2) introduction of the ion having the solvation shell into the solution.

The energy effect of solvation (E) is a complex function of the "ion – dipole" distance f(r), ionized potentials, polarizability, dipole and quadrupole moments, and D of solvent. The sum of energy effects of these stages: 1) is the sum of the energies of the "ion – dipole" and "ion – quadrupole" interactions with solvent molecules (Eᵢ), induction interaction of the ion with the induced moment of the solvent...
molecule (E₂), dispersion interaction (E₃), repulsion of the electron shells of the ion and molecule (E₄) and interactions between solvent molecules in the solvation complex (in the first approximation, this interaction is “dipole – induced dipole”); 2) the energy effect of the 2nd stage is calculated using the Born theory. Equation (4) can be reduced to the form

\[ \Delta G_{\text{const}} = f(r) - \left( 1 - \frac{1}{D} \right) \frac{Z_e^2}{2R} = (E_1 + E_2 + E_3 + E_4) - \left( 1 - \frac{1}{D} \right) \frac{Z_e^2}{2R}, \quad (5) \]

If we neglect the difference between the Gibbs energy at solvation (\( \Delta G_{\text{solv}} \)) and the heat of solvation (\( H_{\text{solv}} \)), then from equation (5) it follows, that in environments, where D is variable under constant \( f(r) \), linearity (\( \Delta G_{\text{solv}} \)) of 1/D should be observed. Difficulties are associated with the use of the Born model [3] and its modifications to describe the solvation of “composite” organic ions, due to the need to determine ionic radii, the charge localization place \( z \), and the way to account of the nonlinear effect.

However, (D) and (μ) often change and are not very suitable as a measure of polarity, since the total number of all interactions between solvent molecules and dissolved contamination is much more extensive and includes non-specific Coulomb and specific (hydrogen, “donor – acceptor” and solvophobic connections) interactions.

Since the reactivity of the solvent is determined by the measure of its strength as a donor or acceptor, Gutmann introduced empirical parameters (donor number DN determined from the enthalpy (H) of the reaction of the formation of complexes with antimony pentachloride in 1,2-dichloroethane and acceptor number AN, determined from chemical shift of phosphorus \( ^{31}\text{P} \) in the NMR spectrum in a diluted solution of triethyl phosphate), characterizing the strength of the donor (DN) and the acceptor (AN) of the electron pair. DN and AN of some solvents are shown in table 2.

**Table 2.** Values (DN, kJ / mol) and (AN) of solvents at room temperature [2].

| Solvent        | DN   | AN  | Solvent        | DN   | AN  |
|----------------|------|-----|----------------|------|-----|
| acetone        | 71.2 | 12.5| formamide      | 100.5| 39.8|
| acetonitrile   | 59.1 | 18.9| hexamethylphosphoric triamide | 162.5| 10.6|
| benzene        | 14.6 | 3.2 | n-hexane       | 0    | 0   |
| benzonitrile   | 49.8 | 15.5| methanol       | 80.0 | 41.5|
| dichloromethane| 4.2  | 20.4| N-methyl-2-pyrromidine | 114.3| 13.3|
| diethyl ether  | 80.5 | 3.9 | nitrobenzene   | 18.4 | 14.8|
| dimethylacetamide | 116.5 | 13.6 | propylene carbonate | 63.4 | 18.3|
| dimethylformamide | 111.5 | 16.0 | pyridine       | 138.5| 14.2|
| dimethyl sulf oxide | 120.8 | 19.3 | carbon tetrachloride | 0    | 8.6 |
| 1,4-dioxane    | 62.0 | 10.8| tetrahydrofuran | 83.7 | 8.0 |
| acetic acid    | 62.9 | 52.9| nitromethane   | 11.3 | 20.5|
| ethanol        | 82.1 | 37.1| water          | 75.4 | 54.8|

Based on these numbers, solvents can be divided into 4 classes: donor solvents (large DN values, small AN); acceptor solvents (small DN, large AN); amphoteric solvents (both large DN and AN); “Inert” solvents (small DN and AN). The main disadvantages of chemical classification by acid-base properties: (DN) and (AN) are identified for a limited number of solvents due to the difficulties of experimental determination, and the uncertainty of the prospects for the distribution of these data to solvent mixtures for analyzing their properties.

2. Experimental method

From the review [10] of the impurities present on the surface of metal optics, it can be assumed that their removal is most effective with a mixture of solvents. Therefore, it is advisable to analyze the parametric theory of solubility [11] as the most promising for choosing both individual solvents to remove certain types of contamination from the surface and predicting the properties of solutions formed.
by the displacement of several solvents.

According to the theory of regular solutions [11], if there are two types of molecules, characterized only by dispersion interaction, then, when they are mixed under conditions of zero value of excess volume \( \Delta V^M = 0 \) and random distribution of molecular orientation (excess entropy of mixing \( \Delta S^M = 0 \)), the cohesion energy of one mole of the resulting liquid mixtures can be expressed as

\[
\begin{align*}
-E^M &= \frac{c_{11} V^2_1 x_1^2 + 2c_{12} V^1_1 V^2_2 x_1 x_2 + c_{22} V^2_2 x_2^2}{V_1 x_1 + V_2 x_2}. \quad (6)
\end{align*}
\]

In this equation, the internal energy \( E^M \) of a two-component solution acts as a quadratic function of volume fractions \( x_i \), the volume \( V_i \) is expressed using the average molar fractions of pure components \( x_i \), \( c_{ij} \) describes the interaction of pairs of molecules \( i-j \), \( c_{11} \) and \( c_{12} \) only temperature functions. or a pure one-component solvent, this expression has the form

\[
E_i = c_i V_i, \quad \text{wherefrom} \quad c_{11} = \frac{-E_i}{V_i}. \quad (7)
\]

Since at the temperature of the liquid phase the cohesion energy can be considered approximately equal to the evaporation energy \( \Delta E_i^V \), then (7) can be rewritten as

\[
c = \frac{\Delta E^V_i}{V}, \quad (8)
\]

where \( V \) - is the molecular volume of the solvent.

Since \( c \) is the cohesion energy per unit volume, it can be called the "specific density of the cohesion energy". There is a strong interaction between the two components in the solution. At the same time, if the molecular volumes \( V \) of both components are significantly different, and the energy of thermal motion is significantly greater than the cohesion energy, we can assume that the entropy of mixing \( \Delta S^M_{FH} \) is maximum, and is determined by the expression Flory-Higgins

\[
\Delta S^M_{FH} = -R \left( \ln \phi_1 + \ln \phi_2 \right), \quad (9)
\]

and the activity of the component "1" can be represented as

\[
\ln a_1 = \ln \phi_1 + \phi_2 \left( 1 - \frac{V_1^*}{V_2^*} \right) + \frac{V_2^* \phi_2 (\delta_1 - \delta_2)^2}{RT}. \quad (10)
\]

Several methods are used to calculate the solubility parameter \( \delta \). For example, the value of evaporation energy and molar volume allows us to calculate the main parameters of the theory of regular solutions – the cohesion energy density and \( \delta \). Taking into account the relationship between energy and latent heat of evaporation \( \Delta H^V_{nap} \) at temperature \( T \), the expression for \( \delta \)

\[
\delta = \left( \frac{\Delta H^V_{nap} - RT}{V^M} \right)^{\frac{1}{2}}, \quad (11)
\]

where \( V^M \) is the molar volume of the component.

An example of the effectiveness of the application \( \delta \) is the interaction between solvents and polymers: since on the surface of metal optics, contaminations with different properties are usually present together, in order to increase the affinity of the solvent medium to contamination \( (A_{ch}) \) and in accordance with economic and technological requirements, it is necessary to use solvent mixtures when cleaning. To calculate \( \delta \) of the mixture of solvents we used the expression [12]

\[
\delta_{cm} = x_1^M V_1^M \delta_1 + x_2^M V_2^M \delta_2 + \ldots + x_n^M V_n^M \delta_n, \quad (12)
\]

where \( x_i^M \) - is the mole fraction of the component, calculated as
\[ x_i = \frac{c_i}{M_i} = \frac{c_1}{M_1} + \frac{c_2}{M_2} + \ldots + \frac{c_i}{M_i}, \quad (13) \]

where \( c_i \) is the concentration of the component, \( \% \); \( M_i \) is the molecular weight.

From (13) it is seen that with equal molar volumes (\( \delta_{cm} \)) - is the additive value. Even with different molar volumes (\( V_M \)), it can be approximately considered, that on the plane with the coordinates of the solubility parameters, the point corresponding to the solubility parameter of the mixture (\( \delta_m \)) lies on the straight line that connects the points with the coordinates of the components. This allows us approximately carry out the selection of the cleaning medium graphically. These techniques make it possible to widely use (\( \delta \)) of different solvents for the choice of detergents for cleaning metal optics from contaminations and for increasing \( A_{ch} \).

Azeotrope mixes characterized by constant composition and boiling point, have the greatest advantage. This reduces the cost and relieves the cleaning of metal optics and solvent regeneration. The properties of the individual solvents and azeotrope compositions based on them, in order of increasing their (\( \delta \)), are given in table 3.

### Table 3. Properties of individual solvents and azeotrope compositions based on them.

| Solvent (azeotrope mixes) | Boiling point of solvent composition, °C | Solubility parameter \( \delta \), J \( 1/2 \) cm \( 3/2 \) |
|--------------------------|-----------------------------------------|---------------------------------------------|
| 1. Freon-114B2           | (47.3)                                  | 14.7                                        |
| 2. (Freon-114B2 - tert-butanol) | 99.0 (49.0)                              | 14.9                                        |
| 3. (Freon-114B2 - acetone) | 97.6 (48.1)                              | 15.1                                        |
| 4. (Freon-113 - tertiary butanol) | 98.0 (47.1)                              | 15.3                                        |
| 5. (Freon-113 – ethanol)  | 96.2 (41.3)                              | 15.9                                        |
| 6. (Freon-113 - acetone)  | 88.9 (44.0)                              | 16.0                                        |
| 7. (Freon-113 - acetone - ethanol) | 86.4; 12.0                              | 16.1                                        |
|                          | (54.1)                                  |                                             |
| 8. (Freon-113 - acetone - ethanol) | 76.1; 21.1(55.2)                      | 16.7                                        |
| 9. (Freon-114B2 - tert-butanol - methylene chloride) | 63.0; 0.5(47.4)                      | 17.3                                        |
| 10. (Freon-14B2 - tert-butanol - methylene chloride) | 53.6; 2.2(36.4)                      | 18.0                                        |
| 11. (Freon-113 - methylene chloride - ethanol) | 49.5; 49.5(36.5)                     | 18.0                                        |
| 12. (Carbon tetrachloride - 2-butanone) | 67.5(73.7)                             | 18.3                                        |
| 13. (Freon 112 - 2-butanone) | 14(79.0)                                | 18.8                                        |
| 14. (Chloroform - acetone) | 63.5, mol % (64.5)                      | 19.3                                        |
| 15. (Carbon tetrachloride - acetone) | 11.5(56.2)                            | 19.7                                        |
| 16. Acetone              | -                                       | 19.8                                        |
| 17. (1,1-Dichloroethane - acetone) | 70.0(57.6)                             | 20.0                                        |
| 18. (Cys-1,2 - dichloroethylene - acetone) | 67.4 mol % (57.7)                      | 20.2                                        |
| 19. (Chloroform - acetone – ethanol) | 47.0; 34.0, % molar (62.2)               | 20.4                                        |
| 20. (Ethanol - 2-butanone) | 50.8(74.3)                              | 22.9                                        |

### 3. Results

In practice, of all the mixtures of solvents, compositions based on freon-114B2, which is relatively inexpensive, low deficient, resistant to decomposition, low toxic and fire-safe, are of the greatest
interest. Other freon’s are either too volatile, or scarce and expensive [13], or contain chlorine atoms, as a result of which they are not stable to decomposition. In addition, the azeotrope mix “freon-114B2 – acetone” (2.4% by weight of acetone (composition 3)) contains the maximum number of fluorine atoms compared with other azeotrope mixes (both in the freon itself - 4 atoms, and in the azeotrope mixes as a whole, due to the relatively small content of the other component). Fluorine compounds adsorbed on the metal during cleaning, due to the high ionization energy, increase the optical damage threshold of metal optics.

This occurs because of the extremely high ionization potential of the fluorine atom (Table 4) and the high ionization energy of compounds containing fluorine (Table 5). During adsorption on the optical surface, fluorine compounds prevent the growth of electron concentration in the space above the surface to the values corresponding to ionized gas, when exposed to laser radiation.

### Table 4. Ionization potentials of some atoms, eV [14].

| Atoms             | F   | C   | H   | Al  | Cu  | Cl  | Mo  | Fe  |
|-------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Ionization potential | 17.423 | 11.260 | 13.599 | 5.986 | 7.726 | 12.968 | 7.10 | 7.893 |

### Table 5. Ionization energy (enthalpy of electron breakaway, or positive ionization, I) for molecules and radicals, eV [14].

| Molecules and radicals | CF₄ | CCl₄ | CH₂⁺ | CH₃⁺ | CH₄ | CH₃CHO |
|-----------------------|-----|------|------|------|-----|--------|
| Ionization energy     | 15.56 | 11.47 | 10.40 | 9.84 | 12.71 | 10.22   |
| Molecules and radicals | C₂H₅OH | CBr₄ | SF₆ | C₂H₂ | C₂H₄ |        |
| Ionization energy     | 10.47 | 11.00 | 16.15 | 11.41 | 10.51 |         |

Even in the presence of a significant emission of electrons in the space directly adjoining to the optical surface of metals, which may occur under certain conditions due to the low work function of electrons from metals, these electrons will be absorbed by freon-114B2, pairs of which will be present in the space above the optical surface as a result of its evaporation under the influence of laser radiation. This is due to the significant electron affinity of both the fluorine and bromine atoms themselves, of which freon-114B2 consists, and of compounds containing these atoms. Data on the electron affinity are presented in tables 6, 7.

### Table 6. Electron affinity (enthalpy of electron addition, or negative ionization, \( A_e \)) for some molecules and radicals [15].

| Molecules and radicals | CBr₄ | CCl₄ | CH₂ | CH₃ | C₂H₄ | SF₆ |
|-----------------------|------|------|-----|-----|------|-----|
| Electron affinity, eV  | -2.04 | -2.12 | +0.95 | -1.08 | 1.81 | -1.48 |

### Table 7. Affinity of atoms to electron (energy released during the formation of a negative ion from a neutral unexcited atom of the element) [15].

| Atoms | C   | Cu  | F   | Cl  | Fe  | Br  | Mo  | Al  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|
| Electron affinity, eV | 1.270 | 1.226 | 3.448 | 3.614 | 0.580 | 3.370 | 1.180 | 0.51 |

A comparison of the parametric theory of solubility with experiment has been carried out for the thermodynamic values of non-polar and low-polar solvents at room temperature: heat capacity at constant pressure (\( \Delta C_p^E \)) is consistent with experimental data, coinciding with an accuracy of 10–20% of thermal energy RT (2.5 kJ / mol at room temperature) for most of the solutions of non-polar solvents. Usually the results do not agree when the maximum value (\( \Delta C_p^E \)) is close to the data for ideal solutions and < 0.2 kJ / mol, which is obviously due to the inapplicability of using the Berthelot approximation.
4. Conclusion

Contaminants on the surface of metal optics (taking into account its corrosive properties) have different physicochemical properties and are present, as a rule, together. Analyzed on the basis of the laws of thermodynamics, methods for the selection of solvents and the experiments performed make it possible to recognize the efficient of using azeotrope mixes when cleaning metal optics from contamination.

A composition of solvents based on azeotrope mixes of freon-114B2 with solvents having a solubility parameter (δ), corresponding to or close to the solubility parameter (δ) of the main (by weight) contaminant or a mixture of contaminants present on the optical surface is proposed.

References

[1] Kaplunov I A, Rogalin V E and Filin S A 2015 Analysis of laser-chemical cleaning of metal surfaces Non-ferrous Metals 1 29

[2] 2003 A short reference-book to physico-chemical quantities (In Russian) 10-th Edition ed A A Ravdel and A M Ponomarev (SPb Ivan Fedorov) p 240

[3] Jayaram B, Sharp K and Honig B 1989 Free Energy Calculations of Ion Hydration: An Analysis of the Born Model in Terms of Microscopic Simulations J. Phys. Chem. 93 4320

[4] Cramer C J and Truhlar D G 1999 Implicit Solvation Models: Equilibria, Structure, Spectra, and Dynamics Chemical Reviews 99 (8) 2161 doi:10.1021/cr960149m. PMID 11849023

[5] Marenich A V and Truhlar D G 2009 Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions J of Physical Chemistry B 113 (18) 6378 doi:10.1021/jp810292n. PMID 19366259

[6] Klamt A and Jonas V 1996 Treatment of outlying charge in continuum solvation models J of Chemical Physics 105 (22) 9972 doi:10.1063/1.472829

[7] Ratkova E L 2015 Solvation Thermodynamics of Organic Molecules by the Molecular Integral Equation Theory: Approaching Chemical Accuracy Chemical Reviews 115 (13) 6312 doi:10.1021/cr5000283. PMID 26073187

[8] Kochurin E A and Zubarev N M 2012 Reduced equations of motion of the interface of dielectric liquids in vertical electric and gravitational elds Phys. Fluids. 24 072101

[9] Purcell E M and Morin D J 2013 Electricity and magnetism 3rd edition (Cambridge University Press) p 853

[10] Filin S A, Rogalin V E, Kaplunov I A and Tretiakov S A 2017 A Brief Review of Methods for Increasing the Service Life of Laser Metal Optics Diagnostics, Resource and Mechanics of materials and structures 4 44

[11] Hildebrand J H 1979 An Improvement in the Theory of Regular Solutions Proc. Natl. Acad. Sci. (USA) 76 12 6040

[12] Drinberg S A and Icko E F 1986 Solvents for paint materials (In Russian) (L. Himiya) p 206

[13] Frank-Kameneckij D A 2008 Microkinetics basics. Diffusion and heat transfer in chemical kinetics (In Russian) 10-th Edition (Dolgoprudnyj Intellekt) p 408

[14] Lidin R A, Andreeva L L and Molochka V A 1987 Inorganic Chemistry Handbook (In Russian) (M Himiya) p 320

[15] 1976 Physical Quantity Tables Reference (In Russian) ed Kikoina I K (M Atomizdat) p 503