Physico-Chemical Properties of Solvents for Cleaning Metal Optics in Order to Increase Its Service Life

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Abstract. Metal mirrors are widely used in IR optics, including high-power lasers, due to the high reflection coefficient. Traditional methods of wiping optical devices are not applicable in this case, due to the formation of scratches caused by the low hardness of metals. Cleaning metal optics from a significant part of organic impurities noticeably increases the service life of high-power laser mirrors. Removing dirt from metal optics is most effective with a mixture of non-aqueous solvents. Methods for selecting solvents, analyzed on the basis of the laws of thermodynamics and experiments carried out, make it possible to recognize that it is advisable, when cleaning mirrors, to use solvent compositions based on azeotropic mixtures with freon-114B2 with a solubility parameter δ corresponding to or close to the solubility parameter δ of the main (by mass) contaminations.

INTRODUCTION

Traditional methods of wiping metal laser mirrors are not applicable, due to the formation of scratches caused by the low hardness of metals [1].

Coulomb ion-ion and ion-dipole interaction plays a main role in electrolyte solutions. For organic compounds, the ionic strength is very small in most cases. To dissolve ionic compounds in the solution [2], the Gibbs energy change ΔG at solvation is:

$$\Delta G = E_1 - E_{\text{interaction ion-dipole}} - E_{dispersion\ interaction} - E_{repulsive\ energy} - E_2 - E_3 - E_o, \tag{1}$$

where E_1 is the heat of evaporation depending on the articulated structure of the solvation complex; the next three components are interpreted according to the Buckingham model [3], without taking into account the quadrupole moment; E_2 is the energy of transition of the ion into the solution (it is assumed that it has an electrostatic nature, that the radius of the solvation ion is equal to the sum of the crystal chemical radius of the ion and the diameter of the water molecule, and that the changes in the dielectric constant of the solvent near the ion are taken into account); E_3 is the hydrogen bond energy; E_0 is the heat of hydration of the inert gas, which is closest in terms of the electronic structure for this ion.

PROBLEM STATEMENT

The model discussed in [2] well reconciles calculated data with experiment for aqueous solutions of some ions. The difficulty is related to the interpretation of ΔG in non-aqueous solvents. The ion bonds based on the dipole moment μ and the dielectric constant D must be taken into account. The constant D shows the following: a change in the electric field strength between the capacitor plates when they are transferred from the vacuum to a solvent; the ability of a solvent to separate electric charges and orient its dipoles; description of the solvation of "composite" organic ions; determination of ionic radii; places of charge localization and the way of accounting for the nonlinear

effect. Therefore, the model reported in [2] is advisable for use when cleaning mirrors with soluble inorganic salts as the predominant contaminations. In non-polar solvent molecules, bias polarization oriented in one direction (orientation polarization) is induced. Therefore, the criterion for dividing solvents into polar and non-polar is the presence or absence of the constant μ in their molecules. However, the values of D and μ in this case often do not change in parallel, Table 1 [4].

TABLE 1. Relative values of D and the constant μ, (C•m) at 20 °C

Solvent	D	$\mu \cdot 10^{-30}$	Solvent	D	$\mu \cdot 10^{-30}$
N-methylformamide	182.4	12.88	acetonitrile	36.0	11.48
formamide	109.5	11.24	methanol	32.7	5.67
H_2O	78.3	6.07	hexamethylphosphoric triamide	29.6	18.48
propylene carbonate	64.4	16.7	tetramethylurea	23.5	11.58
dimethyl sulfoxide	46.7	13.0	1,2-dichloroethane	10.4	6.20

Since the polarity of the solvent is not described using a single physical parameter measurement (D, μ, etc.), it is determined empirically based on the Hammett rule – the concept of linear dependence of ΔG [3].

RESEARCH METHODS

The solvents to remove contaminants from the optical surface of mirrors are proposed to be chosen on the basis of the *solubility parameter* [5] in the parametric theory of regular solutions, based on the concepts of statistical mechanics and the idea of an exactly regular solution in the form of a lattice model proposed by Guggenheim, and the analogy with the Bragg-Williams approximation (zero order) used in the theory of phase transformations of alloys. When discussing the thermodynamic characteristics of the solutions, we used the idea of an ideal solution, in which the molecules of all components have the same size and shape, and the interaction among them is the same. The change in the thermodynamic characteristics of a solution when it is formed from pure components is expressed through the mixing function X^M [6] as

$$X^M = X_{\text{solution}} - \sum_i x_i \cdot X_{i\text{component}}. \tag{2}$$

Then, a solution is called ideal when the following expressions are valid:

$$\Delta G^M = RT \cdot \left(x_1 \cdot \ln x_1 + x_2 \cdot \ln x_2 \right); \tag{3}$$

$$\Delta S^M = -R \cdot \left(x_1 \cdot \ln x_1 + x_2 \cdot \ln x_2 \right); \tag{4}$$

$$\Delta H^M = 0, \quad \Delta V^M = 0, \tag{5}$$

where x is the mole fraction; R is the gas constant; T is temperature; ΔS^M is the ideal entropy of mixing, ΔV^M is the change in the molar volume during mixing; ΔG^M is free energy mixing.

During mixing, ΔS^M always increases, it is independent of the type and combination of components, and it is included in the expression for ΔG^M. Therefore, when discussing real solutions, one can take into account only the difference in changes in the functions, associated only with mixing, as compared with the ideal solution. To express the non-ideality of the solution, the activity coefficient γ and the excess thermodynamic function X^E are used,

$$X^E = \Delta X^M - \Delta X^M_{\text{ideal solution}}. \tag{6}$$

Then the equation for a two-component mixture can be written as:

$$\Delta G^M = RT \cdot \left(x_1 \cdot \ln \gamma_1 + x_2 \cdot \ln \gamma_2 \right); \tag{7}$$

$$\Delta S^M = -R \cdot \left(x_1 \cdot \ln \gamma_1 + x_2 \cdot \ln \gamma_2 \right). \tag{8}$$

When studying the chemical nature of solution non-ideality, the main task is theoretical-experimental assessment, reducible to finding the relationship of γ and ΔG^E with the properties of the solution components and to determining the temperature and pressure dependences of the values in equations (7, 8):

$$\Delta G^E = Ax_1 \cdot x_2. \tag{9}$$

The coefficient A may take negative/positive values, and it is independent of temperature. These mixtures of molecules of the same kind are considered as *regular solutions*, this being confirmed in many experiments. If the

molar volumes of the two components are different, the form of equation (9) is preserved in practical calculations. The following expression is introduced, where A is the exchange interaction energy ω:

$$\Delta G^E = \omega x_1 \cdot x_2, \partial de\left(\omega > 0\right). \tag{10}$$

However, the findings of Guggenheim did not explain with what properties of the solution components the quantity ω is related. According to [5], the volume is expressed through the average mole fractions of pure components ($\Delta G^E = 0$) and, practically, in a similar form through the Van der Waals equation. The term c_{ij} describes the interaction of pairs of molecules (i-j); (c_{11}) and (c_{12}) are functions of temperature only. For a pure fluid consisting of one component, $\Delta E_1 = c_{11}V_1$, or

$$c_{11} = \frac{-E_1}{V_1}. \tag{11}$$

The internal mixing energy ΔU^M can be defined as:

$$\Delta U^M = U_{12} - \left(x_1 \cdot U_1 + x_2 \cdot U_2\right). \tag{12}$$

If we introduce the volume fraction φ and, taking into account that $\Delta U^M = 0$ for an ideal gas, determine ΔU^M from equations (11) and (12), we obtain:

$$\Delta U^M = \left(c_{11} + c_{22} - 2c_{12}\right) \cdot \varphi_1 \cdot \varphi_2 \cdot \left(x_1 \cdot V_1 + x_2 \cdot V_2\right). \tag{13}$$

In accordance with the geometric average rule, c_{12} is approximately determined from the London dispersion interaction equation, providing that the difference in ionization energies can be neglected. This actually corresponds to the Berthelot principle used as a rule for combining the parameters of the potential energy of molecules:

$$c_{12} = \left(c_{11} \cdot c_{22}\right)^2. \tag{14}$$

Substituting expression (14) into expression (12), we obtain:

$$\Delta U^M = \left(\delta_1 - \delta_2\right)^2 \cdot \varphi_1 \cdot \varphi_2 \cdot \left(x_1 \cdot V_1 + x_2 \cdot V_2\right), \tag{15}$$

where the solubility parameter δ is defined as:

$$\delta = c^{\frac{1}{2}} = \left(\frac{\Delta E^V}{V}\right)^{\frac{1}{2}}. \tag{16}$$

Using this theory, we obtain expressions for other thermodynamic functions, assuming that regular solutions are characterized by zero mixing entropy ($\Delta S^E = 0$); then $\Delta H^E = \Delta U^E$ since $\Delta V^E = 0$ and $\Delta G^E = \Delta U^E$. The calculation of the activity coefficient γ and ΔG^E is practically limited by the choice of the value of ΔE^M. Then, in accordance with the parametric theory of solubility (PTS), γ is determined from the system of equations:

$$\begin{cases} RT \cdot \ln\left(\dfrac{a_2}{x_2}\right) = RT \cdot \ln \gamma_2 = V_2 \cdot \varphi_1^2 \cdot \left(\delta_1 - \delta_2\right)^2 \\ RT \cdot \ln\left(\dfrac{a_1}{x_1}\right) = RT \cdot \ln \gamma_1 = V_1 \cdot \varphi_2^2 \cdot \left(\delta_1 - \delta_2\right)^2 \end{cases}. \tag{17}$$

The partial molar free energy ΔG^M for component "1" is

$$\Delta G^M = RT \cdot \ln a_1 = RT \cdot \ln x_1 + V_1 \cdot \varphi_2^2 \cdot \left(\delta_1 - \delta_2\right)^2. \tag{18}$$

The theory of regular solutions allows us to determine the conditions for optimal mixing of 2 chemically non-interacting non-polar liquids from the equation:

$$\Delta F_V^{mixture} = \left(x_1 \cdot \varphi_1 + x_2 \cdot \varphi_2\right) \cdot \left(\delta_1 - \delta_2\right)^2 \cdot \varphi_1 \cdot \varphi_2 + RT \cdot \left(x_1 \cdot \ln x_1 + x_2 \cdot \ln x_2\right), \tag{19}$$

where x_1 and x_2 are the mole fractions of components; φ_1 and φ_2 are the volume fractions of components; $\Delta F_V^{mixture}$ is free mixing energy.

The minimum value of $\Delta F_V^{mixture}$ when mixed in the system is achieved with equal δ of the components. In practice $\gamma \geq 1$ (the equation (17)), only positive deviations of the solution from ideality are observed. The mutual

solubility of the components of the solution is determined by the difference in the specific densities of the cohesive energy due to the existence of only dispersive forces (the Berthelot rule); therefore, the restriction for ω is reasonable.

The approach to δ is basically "physical", but the introduction of specific components of the interaction gives it a balanced position, except the case that solvation plays a decisive role. When considering intermolecular interaction from a macroscopic point of view, δ is close to internal pressure $P_i = \left(\dfrac{\partial U}{\partial V}\right)_T$. In terms of thermodynamics, P_i has considerable versatility and exceeds δ; however, for simple molecules, we can expect their interrelation ($P_i \approx \delta^2$).

The temperature dependence of δ is almost invisible. Generally, δ is determined at 25 °C with the application of different calculation methods (ΔH_{nap}^V), for example, the calorimetric method. The Hildebrand method [6] of the experimental estimation of δ is based on the constancy of evaporation entropy, dependencies for internal pressure, critical parameters, surface tension, etc. A semi-empirical method is one which assumes that a good solvent for a non-electrolytic solute (polymer) is a compound that has the value of δ close to the solubility parameter of this substance. This is justified by the fact that, in order to ensure dissolution, the Gibbs mixing energy in the process operating under a constant pressure P must be negative, and this can be achieved by decreasing ΔH_p. If ΔH_p is negative/positive and less than the value of $T\Delta S_P$, mixing may occur. For non-polar liquids, this is equivalent to a decrease in $(\delta_A - \delta_B)^2$.

This theory was extended to systems containing substances with polar and associated molecules. Prauznits [5] and Gordon [7] divided the quantity δ into two components related to dispersion $\delta_d(\lambda)$ (nonpolar component of δ) and dipole $\delta_p(\tau)$ (polar component of δ) interactions, each of which is determined separately as:

$$\delta^2 = \frac{\Delta E^V}{V} = \delta_d^2 + \delta_p^2. \tag{20}$$

Prauznits determined these parameters for non-associated polar solvents and used them for a two-component solution consisting of polar "1" and non-polar "2" molecules. For component "1", the specific energy density of the cohesion is equal to:

$$c_{11} = \frac{\left(\Delta U_1\right)_{vapour}}{V_1^{\circ}} = \tau_1^2 + \lambda_1^2; \tag{21}$$

$$c_{22} = \frac{\left(\Delta U_2\right)_{vapour}}{V_2^{\circ}} = \lambda_2^2; \tag{22}$$

$$c_{12} = \lambda_1 \cdot \lambda_2 + \psi_{12}, \tag{23}$$

where for component "2", $\lambda_2 = \delta_2$; ψ_{12} is the specific energy density associated with induction forces between the two components, and it is constant.

Herefrom, ΔG_P^E can be calculated as:

$$\Delta G_P^E = \left(c_{11} + c_{22} - 2c_{12}\right) \cdot \varphi_1 \varphi_2 \cdot \left(x_1 V_1^{\circ} + x_2 V_2^{\circ}\right) = \left[\left(\lambda_1 - \lambda_2\right)^2 + \tau_1^2 - 2\psi_{12}\right] \cdot \varphi_1 \varphi_2 \cdot \left(x_1 V_1^{\circ} + x_2 V_2^{\circ}\right). \tag{24}$$

In equation (24) Prauznits estimated the values of the polar τ_1 and nonpolar λ_1 components of δ using the general concept of the homomorphism of polar molecules. Then, using the Flory-Higgins ratio, if we apply the empirical dependence $\psi_{12} = KT^2$ ($K = 0.4$–0.45), we can calculate γ for substances with nonpolar molecules in a polar solvent and determine the correctness of the solvent choice asfollows:

$$\left(RT \cdot \ln \gamma_2\right)_{x_2 \to 0} = V_2^{\circ} \cdot \left[\left(\lambda_1 - \lambda_2\right)^2 + \tau_1^2 - 2\psi_{12}\right] + RT \cdot \left(\ln \frac{V_2^{\circ}}{V_1^{\circ}} + 1 - \frac{V_2^{\circ}}{V_1^{\circ}}\right) =$$

$$= V_2^{\circ} \cdot \left[\left(\delta_d\right)_1 - \left(\delta_d\right)_2\right]^2 + \left(\delta_p\right)_1^2 - 2\psi_{12} + RT \cdot \left(\ln \frac{V_2^{\circ}}{V_1^{\circ}} + 1 - \frac{V_2^{\circ}}{V_1^{\circ}}\right). \tag{25}$$

In equations (24) and (25), associated liquids with hydrogen bonds, such as alcohols and organic acids, the specific nature of the interaction which cannot be expressed fully enough with the help of δ_d and δ_p, were excluded from consideration. It follows from PTS that the dissolution will occur at any ratios of the components if the molar enthalpy of mixing (ΔH) will be close to "0" in the equation

$$\Delta H = \left(\delta_1 - \delta_2\right)^2 \cdot V_1 \cdot \varphi_1 \cdot \varphi_2 = \beta \cdot V_1 \cdot \varphi_1 \cdot \varphi_2, \tag{26}$$

where **β** is the compatibility parameter pointing to the affinity of the blending components.

FINDINGS

Polymerized contaminants, usually including most of the all contaminants, are the most difficult to clean of all possible contaminants present on the mirror; therefore, the above example of the solvent–polymer interaction using δ is of practical importance. A significant advantage in choosing solvents for cleaning mirrors is the ability to predict the properties of both individual solvents and their mixtures. In practice, in the optical and microelectronic industries, the fire risk of highly polar organic solvents, insufficient inertness to water and metals, the damaging effects of chlorine-containing freons on the ozone layer of the Earth, the high cost and deficiency of freons are the main reasons for the transition to compositions based on fluorine-substituted hydrocarbons. This is due to their high dissolving ability and higher inertness (compared to chlorine-containing) to water and metals at 25 ºC. Therefore, non-aqueous compositions based on freon-114B2 are of particular interest. They form azeotropes with δ corresponding to or close to δ of the main (by mass) contaminants present on the mirror.

CONCLUSIONS

1. Although the PTS is based on the concept of dispersion forces and the Berthelot rule and extends accordingly to non-polar molecular solutions, the experiments carried out in [8] satisfactorily confirmed that it is also applicable to solids and polar liquids (the similarity in the values of δ gives a more negative Gibbs mixing energy, providing mutual mixing of substances). With some refinements and additions, the use of a simpler mathematics than, e.g., the theory of solvation, fluid state and solutions, etc., the PTS in many cases offers a better agreement with experimental data. The method of one parameter (δ) is applicable even in the presence of strong polar interactions and hydrogen bonds in the component.

2. The solvent selection methods analyzed based on the laws of thermodynamics and the experiments performed have shown that the removal of contaminants with different physicochemical properties and located, as a rule, together on the surface of metal optics (in view of its corrosive properties), is most effective by freon-114B2-based compositions.

3. The results on cleaning the optical surface from a considerable part of contaminants make it possible to increase the service life of high-power laser mirrors. They can also be applied to cleaning precision metal parts used in other industries.

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