

**ON THE DEFINITION OF SCALES
IN VAN OSS-CHAUDHURY-GOOD ACID-BASE THEORY**

by

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Abstract

Acid-base components of van Oss-Chaudhury-Good theory for surface energetics are extrathermodynamical parameters whose direct measurement cannot be performed. Estimates of acid-base components are obtained by solving the model equations of the theory, which involve the experimental assessment of liquid surface tensions and contact angles for appropriate liquid-solid pairs. Due to symmetries implicit in the mathematical form of such model equations, theory admits a triple infinity of formally equivalent scales, with the same prediction ability. This entails, in particular, the impossibility of interpreting acid-base components in a strictly direct way. In this note we illustrate a way to select an univocal vOCG scale by an essentially conventional assignment of the component values for suitably chosen reference materials. The extension of the same procedure is outlined for a more general class of multicomponent models, of which vOCG theory is a very particular case.

1. Introduction

Multicomponent theories play an important role in modeling the interfacial interactions of many materials and more specifically in the prediction of the solid-liquid adhesion work and surface free energy of solid surfaces. The strategy of describing the surface interactions of two materials by means of an appropriate number of “components”, pertaining to contributions of different physico-chemical nature, is shared by a lot of models proposed through the years. Van Oss-Chaudhury-Good (vOCCG) acid-base theory^[1–6] constitutes one of the most known and successful multicomponent models; it expresses the work of adhesion of a liquid l on a solid s as

$$W^{\text{adh}} = 2 \left[\sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+} \right] \quad (1.1)$$

while the surface tension of the liquid and the surface free energy of the solid are respectively written as

$$\gamma_l = \gamma_l^{LW} + 2\sqrt{\gamma_l^+ \gamma_l^-} \quad \gamma_s = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \gamma_s^-}, \quad (1.2)$$

on having denoted with the superscript LW the Lifshitz-van del Waals components of the materials, related to dispersive interactions, and with $+$ and $-$ respectively the acidic and the basic components, which take into account the acid-base interactions between electron-donor (basic) and electron-acceptor (acidic) sites of the molecules involved. Through the geometrical means of basic components with acidic components, all the model equations reflect the intrinsic complementarity of acid-base interactions, acidity and basicity being obviously understood in a wide Lewis' sense. Acid-base components cannot be measured in a direct way and at the moment *no significant and convincing correlation with some absolute scale of acid-base behaviour is recognized*, although some indication has been given in the literature that the acidic component of water is 3.2 to 5.5 times the basic one^[7–9].

It is known^[7,8] that equations (1.1)-(1.2) are invariant under appropriate linear transformations of acid-base components. These linear transformations form a group with respect to composition, which means that the corresponding representation matrices constitute a nonabelian group when endowed with the usual matrix multiplication — see Theorem 1 in Section 2. Such a simple remark has important consequences, since it entails that the only experimental measurement of surface tensions and adhesion works does not determine vOCG components in a unique way. Model equations (1.1)-(1.2) are intrinsically compatible with a multiplicity of “scales” of acid-base components, each obtainable from each other by a suitable transformation of the invariance group, and all in principle equivalent as for prediction ability. In the present note we address the problem of determining a univocal vOCG acid-base scale, manipulating the acid-base components of some appropriately chosen reference compounds by means of suitable transformations of the invariance group.

The plan of the paper is the following: the main theoretical results concerning the structure of the invariance group transformations are stated and proved in Section 2; application to the problem of scale selection in vOCG theory is faced up in Section 3; finally, the more general category of quadratic multicomponent theories is introduced in Section 4, and the related problem of scale selection addressed in Section 5.

2. Analytical results

VOCG theory states that for each liquid (or solid) a triplet of components, γ_l^{LW} , γ_l^+ and γ_l^- (respectively, γ_s^{LW} , γ_s^+ , γ_s^-), can be defined in such a way that the surface free energy of the material can be written according to (1.2) and the corresponding liquid-solid adhesion work takes the form (1.1). By Young-Dupré equation we obtain then

$$\gamma_l(1 + \cos \theta) = 2[\sqrt{\gamma_l^{LW}\gamma_s^{LW}} + \sqrt{\gamma_l^+\gamma_s^-} + \sqrt{\gamma_l^-\gamma_s^+}] \quad (2.1)$$

where θ is the equilibrium contact angle of the pair. Let \mathbb{L} and \mathbb{S} be two sets of $L \geq 1$ liquids and $S \geq 1$ solids, respectively; each liquid is denoted with a value of the index $i = 1, \dots, L$, whereas an index $j = 1, \dots, S$ distinguishes the different solids. The components of the i -th liquid will be then written as

$$\gamma_{l,i}^{LW} \quad , \quad \gamma_{l,i}^+ \quad , \quad \gamma_{l,i}^-$$

and a similar notation will be introduced for the corresponding components of the j -th solid

$$\gamma_{s,j}^{LW} \quad , \quad \gamma_{s,j}^+ \quad , \quad \gamma_{s,j}^- .$$

Equations (1.2) and (1.1) trivially generalize to any liquid, solid, and liquid-solid pair:

$$\gamma_{l,i} = \gamma_{l,i}^{LW} + 2\sqrt{\gamma_{l,i}^+ \gamma_{l,i}^-} \quad \forall i = 1, \dots, L \quad \gamma_{s,j} = \gamma_{s,j}^{LW} + 2\sqrt{\gamma_{s,j}^+ \gamma_{s,j}^-} \quad \forall j = 1, \dots, S$$

$$W_{i,j}^{\text{adh}} = \gamma_{l,i}(1 + \cos \theta_{i,j}) = 2\left[\sqrt{\gamma_{l,i}^{LW} \gamma_{s,j}^{LW}} + \sqrt{\gamma_{l,i}^+ \gamma_{s,j}^-} + \sqrt{\gamma_{l,i}^- \gamma_{s,j}^+}\right] \quad \forall i, j ,$$

provided that $\theta_{i,j}$ and $W_{i,j}^{\text{adh}}$ are taken as the contact angle and the adhesion work of the i -th liquid on the j -th solid. The previous equalities can be usefully put into a matrix form

$$\gamma_{l,i} = X_i^T R X_i \quad \forall i = 1, \dots, L \quad \gamma_{s,j} = Y_j^T R Y_j \quad \forall j = 1, \dots, S$$

$$W_{i,j}^{\text{adh}} = \gamma_{l,i}(1 + \cos \theta_{i,j}) = 2X_i^T R Y_j \quad \forall i, j \tag{2.2}$$

by posing, for each i and j ,

$$X_i = \begin{pmatrix} \sqrt{\gamma_{l,i}^{LW}} \\ \sqrt{\gamma_{l,i}^+} \\ \sqrt{\gamma_{l,i}^-} \end{pmatrix} \quad Y_j = \begin{pmatrix} \sqrt{\gamma_{s,j}^{LW}} \\ \sqrt{\gamma_{s,j}^+} \\ \sqrt{\gamma_{s,j}^-} \end{pmatrix} \quad R = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{2.3}$$

and denoting with the superscript T the transpose of an arbitrary matrix — it is understood that the dispersive, acidic and basic components of any material are always nonnegative. In the set (2.2) of $LS+L+S$ equations, the $3L+4S$ variables $\gamma_{l,i}^{LW}$, $\gamma_{l,i}^+$, $\gamma_{l,i}^-$ and $\gamma_{s,j}$, $\gamma_{s,j}^{LW}$, $\gamma_{s,j}^+$,

$\gamma_{s,j}^-$ must be regarded as unknowns. Only the total surface tensions $\gamma_{l,i}$ of liquids can be measured independently and are taken as given parameters, together with the equilibrium contact angles $\theta_{i,j}$. For L, S sufficiently large we obtain $LS + L + S > 3L + 4S$ and (2.2) turns out to be an overdetermined set of nonlinear equations, to be solved by means of some best-fit algorithm. The research of any best-fit solution implies the optimization of some merit function V dependent on the rests

$$\begin{aligned} \Delta_{l,i} &= X_i^T R X_i - \gamma_{l,i} & \Delta_{s,j} &= Y_j^T R Y_j - \gamma_{s,j} \\ \Delta_{i,j} &= X_i^T R Y_j - \frac{1}{2}(1 + \cos \theta_{i,j})\gamma_{l,i}. \end{aligned} \tag{2.4}$$

Existence of best-fit solutions for V is highly nontrivial, since no general argument can be easily invoked. In any case, uniqueness of such solutions is excluded by the following theorem, whose proof is immediate^[7,8].

Theorem 1

Let $A_i, i = 1, \dots, L$, and $B_j, j = 1, \dots, S$ be some — real or complex — 3×3 nonsingular matrices such that the substitutions $X_i \rightarrow A_i X_i$ and $Y_j \rightarrow B_j Y_j$ leave each of the rests (2.4) invariant. Then:

- (i) $A_i = B_j = C \forall i = 1, \dots, L, j = 1, \dots, S$, where C is any matrix satisfying $C^T R C = R$;
- (ii) the set \mathbb{G}_3 of matrices C as above constitutes a group with respect to the usual matrix product. Such a group is isomorphic to the orthogonal group $O(2, 1; \mathbb{C})$, and its intersection with the the group $Gl(3, \mathbb{R})$ of real 3×3 invertible matrices is isomorphic to the orthogonal group $O(2, 1; \mathbb{R})$.

The lack of uniqueness for the best-fit solution easily follows because invariance of all the rests implies invariance of V .

Theorem 2

The group \mathbb{G}_3 includes the 3-parameter family of nonsingular matrices

$$\pm \exp[\omega_1 E_1 + \omega_2 E_2 + \omega_3 E_3] \quad \forall \omega_1, \omega_2, \omega_3 \in \mathbb{C} ,$$

where

$$E_1 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} \quad E_2 = \begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad E_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} .$$

Proof

Since $C \in \mathbb{G}_3$ is nonsingular, a complex 3×3 matrix E exists such that

$$C = \exp(E) = \sum_{n=0}^{\infty} \frac{1}{n!} E^n$$

and, due to $R^2 = \mathbb{I}$, the condition $C^T R C = R$ assumes the equivalent form

$$\exp(RE^T R) = \exp(-E) . \tag{2.5}$$

Equation (2.5) is certainly verified if $RE^T R = -E$, i.e.

$$E^T R = -RE \quad \iff \quad (RE)^T = -RE ,$$

which implies that RE is a skew-symmetric matrix

$$RE = \Omega = \begin{pmatrix} 0 & \omega_1 & \omega_2 \\ -\omega_1 & 0 & -\omega_3 \\ -\omega_2 & \omega_3 & 0 \end{pmatrix} \quad \omega_1, \omega_2, \omega_3 \in \mathbb{C} .$$

As a consequence, the matrix E is given by

$$E = R\Omega = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & \omega_1 & \omega_2 \\ -\omega_1 & 0 & -\omega_3 \\ -\omega_2 & \omega_3 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \omega_1 & \omega_2 \\ -\omega_2 & \omega_3 & 0 \\ -\omega_1 & 0 & -\omega_3 \end{pmatrix}$$

and can be rewritten as

$$E = \omega_1 E_1 + \omega_2 E_2 + \omega_3 E_3 ,$$

so that

$$C = \exp(E) = \exp[\omega_1 E_1 + \omega_2 E_2 + \omega_3 E_3] .$$

The final result follows by observing that $C^T R C = R$ implies $(-C)^T R (-C) = R$. \square

A useful by-product is the following corollary.

Corollary 2.1

For any $\omega \in \mathbb{C}$ there holds

$$\begin{aligned} \exp(\omega E_1) &= \begin{pmatrix} 1 & \omega & 0 \\ 0 & 1 & 0 \\ -\omega & -\omega^2/2 & 1 \end{pmatrix} & \exp(\omega E_2) &= \begin{pmatrix} 1 & 0 & \omega \\ -\omega & 1 & -\omega^2/2 \\ 0 & 0 & 1 \end{pmatrix} \\ \exp(\omega E_3) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & e^\omega & 0 \\ 0 & 0 & e^{-\omega} \end{pmatrix} . \end{aligned}$$

Proof

The expression for $\exp(\omega E_1)$ is easily deduced from the definition, by taking into account that E_1 is a nilpotent matrix:

$$\exp(\omega E_1) = \sum_{n=0}^{\infty} \frac{\omega^n}{n!} E_1^n = \mathbb{I} + \omega \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} + \frac{\omega^2}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} .$$

The immediate equality $E_2 = -E_1^T$ leads to

$$\exp(\omega E_2) = \exp(-\omega E_1^T) = [\exp(-\omega E_1)]^T$$

and provides the second expression. As for $\exp(\omega E_3)$, the computation is straightforward — it concerns the exponential of a diagonal matrix. \square

Theorem 2 can be applied to prove the statement below, about the possibility of redefining acid-base components for a particular liquid or solid.

Theorem 3

Let γ_0^{LW} , γ_0^+ , γ_0^- be the nonnegative acid-base components of a given material, with $\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-} > 0$. Consider the new set of components γ^{LW} , γ^+ , γ^- , defined by means of

$$\begin{pmatrix} \sqrt{\gamma^{LW}} \\ \sqrt{\gamma^+} \\ \sqrt{\gamma^-} \end{pmatrix} = C \begin{pmatrix} \sqrt{\gamma_0^{LW}} \\ \sqrt{\gamma_0^+} \\ \sqrt{\gamma_0^-} \end{pmatrix} \quad \text{with} \quad C^T RC = R.$$

Then, $\forall \xi \in [0, 1]$ and $\eta \in \mathbb{R}$ a matrix C exists such that

$$\begin{aligned} \gamma^{LW} &= [\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}]\xi \\ \gamma^+ &= [\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}]\frac{1-\xi}{2}e^\eta \\ \gamma^- &= [\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}]\frac{1-\xi}{2}e^{-\eta}. \end{aligned} \tag{2.6}$$

Moreover, a suitable choice of C leads to either $\gamma^+ = 0$ or $\gamma^- = 0$.

Proof

We firstly show that the dispersive and polar contributions to surface free energy, γ^{LW} and $2\sqrt{\gamma^+}\sqrt{\gamma^-}$ respectively, can take the values

$$\gamma^{LW} = \xi[\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}] \quad 2\sqrt{\gamma^+}\sqrt{\gamma^-} = (1-\xi)[\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}] \tag{2.7}$$

for any $\xi \in [0, 1]$. To this end, we subdivide the proof in three parts and distinguish the cases where γ_0^+ and γ_0^- are both zero or not.

Suppose that $\gamma_0^+ > 0$ and apply Corollary 2.1 to obtain, $\forall \omega_1 \in \mathbb{R}$,

$$\begin{pmatrix} \sqrt{\gamma^{LW}} \\ \sqrt{\gamma^+} \\ \sqrt{\gamma^-} \end{pmatrix} = \exp(\omega_1 E_1) \begin{pmatrix} \sqrt{\gamma_0^{LW}} \\ \sqrt{\gamma_0^+} \\ \sqrt{\gamma_0^-} \end{pmatrix} = \begin{pmatrix} \sqrt{\gamma_0^{LW}} + \omega_1 \sqrt{\gamma_0^+} \\ \sqrt{\gamma_0^+} \\ \sqrt{\gamma_0^-} - \omega_1 \sqrt{\gamma_0^{LW}} - \omega_1^2 \sqrt{\gamma_0^+}/2 \end{pmatrix}. \tag{2.8}$$

The polynomial

$$P(\omega_1) = -\omega_1^2 \frac{\sqrt{\gamma_0^+}}{2} - \omega_1 \sqrt{\gamma_0^{LW}} + \sqrt{\gamma_0^-}$$

has a maximum in $\omega_1 = -\sqrt{\gamma_0^{LW}}/\sqrt{\gamma_0^+}$, where it takes the value

$$P(-\sqrt{\gamma_0^{LW}}/\sqrt{\gamma_0^+}) = \frac{\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}}{2\sqrt{\gamma_0^+}} > 0.$$

The zeroes of P are the solutions of the equation

$$-\omega_1^2 \frac{\sqrt{\gamma_0^+}}{2} - \omega_1 \sqrt{\gamma_0^{LW}} + \sqrt{\gamma_0^-} = 0$$

which provides

$$\omega_1 = \begin{cases} \nearrow -\frac{\sqrt{\gamma_0^{LW}} + \sqrt{\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}}}{\sqrt{\gamma_0^+}} = -\omega_1^* < 0 \\ \searrow \frac{-\sqrt{\gamma_0^{LW}} + \sqrt{\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}}}{\sqrt{\gamma_0^+}} = 2\frac{\sqrt{\gamma_0^-}}{\sqrt{\gamma_0^+}} \frac{1}{\omega_1^*} > 0 \end{cases}$$

and since $\sqrt{\gamma^-} \geq 0$ in (2.8), we deduce that ω_1 must be chosen as follows

$$-\omega_1^* \leq \omega_1 \leq 2\frac{\sqrt{\gamma_0^-}}{\sqrt{\gamma_0^+}} \frac{1}{\omega_1^*}.$$

The analogous condition $\sqrt{\gamma^{LW}} \geq 0$ in (2.8) requires $\omega_1 \geq -\sqrt{\gamma_0^{LW}}/\sqrt{\gamma_0^+}$, so that

$$-\frac{\sqrt{\gamma_0^{LW}}}{\sqrt{\gamma_0^+}} \leq \omega_1 < 2\frac{\sqrt{\gamma_0^-}}{\sqrt{\gamma_0^+}} \frac{1}{\omega_1^*}, \tag{2.9}$$

because of the trivial inequality $\omega_1^* \geq 2\sqrt{\gamma_0^{LW}}/\sqrt{\gamma_0^+}$. In the interval (2.9) the square root $\sqrt{\gamma^-}$ can assume any value from 0 to $P(-\sqrt{\gamma_0^{LW}}/\sqrt{\gamma_0^+}) = [\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}]/2\sqrt{\gamma_0^+}$.

More precisely, for any given $\xi \in [0, 1]$ there exists a unique ω_1 such that

$$\sqrt{\gamma^-} = (1 - \xi) \frac{\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}}{2\sqrt{\gamma_0^+}};$$

correspondingly, $\sqrt{\gamma^+} = \sqrt{\gamma_0^+}$ and

$$2\sqrt{\gamma^+}\sqrt{\gamma^-} = (1 - \xi)[\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}], \quad (2.10)$$

whereas

$$\gamma^{LW} = \gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-} - 2\sqrt{\gamma^+}\sqrt{\gamma^-} = \xi[\gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}]. \quad (2.11)$$

This proves (2.7) for $\gamma_0^+ > 0$. Notice that $[0, \gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}]$ is the widest interval of definition for both γ^{LW} and $2\sqrt{\gamma^+}\sqrt{\gamma^-}$, since $\gamma^{LW} + 2\sqrt{\gamma^+}\sqrt{\gamma^-} = \gamma_0^{LW} + 2\sqrt{\gamma_0^+}\sqrt{\gamma_0^-}$ and the square roots of the new components must be nonnegative anyway.

The case $\gamma_0^- > 0$ can be treated in a similar way by means of the transformation

$$\begin{pmatrix} \sqrt{\gamma^{LW}} \\ \sqrt{\gamma^+} \\ \sqrt{\gamma^-} \end{pmatrix} = \exp(\omega_2 E_2) \begin{pmatrix} \sqrt{\gamma_0^{LW}} \\ \sqrt{\gamma_0^+} \\ \sqrt{\gamma_0^-} \end{pmatrix} = \begin{pmatrix} \sqrt{\gamma_0^{LW}} + \omega_2 \sqrt{\gamma_0^-} \\ \sqrt{\gamma_0^+} - \omega_2 \sqrt{\gamma_0^{LW}} - \omega_2^2 \sqrt{\gamma_0^-} / 2 \\ \sqrt{\gamma_0^-} \end{pmatrix}, \quad (2.12)$$

with $\omega_2 \in \mathbb{R}$. If both γ_0^+ and γ_0^- vanish, we simply have to observe that

$$\exp(\omega_1 E_1 + \omega_2 E_2) = \mathbb{I} + \omega_1 E_1 + \omega_2 E_2 + o(\sqrt{\omega_1^2 + \omega_2^2}) \quad (\omega_1, \omega_2) \in \mathbb{R}^2 \rightarrow (0, 0)$$

and introduce the transformation

$$\begin{aligned} \begin{pmatrix} \sqrt{\gamma^{LW}} \\ \sqrt{\gamma^+} \\ \sqrt{\gamma^-} \end{pmatrix} &= \exp(\omega_1 E_1 + \omega_2 E_2) \begin{pmatrix} \sqrt{\gamma_0^{LW}} \\ \sqrt{\gamma_0^+} \\ \sqrt{\gamma_0^-} \end{pmatrix} = \\ &= \begin{pmatrix} 1 & \omega_1 & \omega_2 \\ -\omega_2 & 1 & 0 \\ -\omega_1 & 0 & 1 \end{pmatrix} \begin{pmatrix} \sqrt{\gamma_0^{LW}} \\ 0 \\ 0 \end{pmatrix} + o(\sqrt{\omega_1^2 + \omega_2^2}) = \sqrt{\gamma_0^{LW}} \begin{pmatrix} 1 \\ -\omega_2 \\ -\omega_1 \end{pmatrix} + o(\sqrt{\omega_1^2 + \omega_2^2}). \end{aligned}$$

The choice of $\omega_1, \omega_2 < 0$ sufficiently close to zero yields positive square roots $\sqrt{\gamma^+}$ and $\sqrt{\gamma^-}$, so that we are led to the previous cases — both acidic and basic components are strictly positive.

Corollary 2.1 allows now to vary the polar components by means of the substitution

$$\begin{pmatrix} \sqrt{\gamma^{LW}} \\ \sqrt{\gamma^+} \\ \sqrt{\gamma^-} \end{pmatrix} \longrightarrow \exp(\omega_3 E_3) \begin{pmatrix} \sqrt{\gamma^{LW}} \\ \sqrt{\gamma^+} \\ \sqrt{\gamma^-} \end{pmatrix} = \begin{pmatrix} \sqrt{\gamma^{LW}} \\ e^{+\omega_3} \sqrt{\gamma^+} \\ e^{-\omega_3} \sqrt{\gamma^-} \end{pmatrix} \quad \omega_3 \in \mathbb{R} .$$

For instance, in the case $\gamma_0^+ > 0$ the final transformation assumes the form

$$\begin{pmatrix} \sqrt{\gamma^{LW}} \\ \sqrt{\gamma^+} \\ \sqrt{\gamma^-} \end{pmatrix} = \begin{pmatrix} \sqrt{\xi} \sqrt{\gamma_0^{LW} + 2\sqrt{\gamma_0^+} \sqrt{\gamma_0^-}} \\ e^{+\omega_3} \sqrt{\gamma_0^+} \\ e^{-\omega_3} (1 - \xi) [\gamma_0^{LW} + 2\sqrt{\gamma_0^+} \sqrt{\gamma_0^-}] / 2\sqrt{\gamma_0^+} \end{pmatrix}$$

and coincides with (2.6) by posing

$$\eta = 2\omega_3 - \ln \left[\frac{1 - \xi \gamma_0^{LW} + 2\sqrt{\gamma_0^+} \sqrt{\gamma_0^-}}{2\gamma_0^+} \right]$$

whenever $\xi \neq 1$. If $\xi = 1$ we get $\gamma^- = 0$, as requested. An analogous result can be established by starting from equation (2.12), with the only difference that $\gamma^+ = 0$ for an appropriate value of the parameter ω_2 . \square

Remark

For any given vector $(\sqrt{\gamma_0^{LW}} \sqrt{\gamma_0^+} \sqrt{\gamma_0^-})^T$ satisfying $\gamma_0^{LW} + 2\sqrt{\gamma_0^+} \sqrt{\gamma_0^-} > 0$ it is always possible to perform a linear transformation $C = \exp(\omega_1 E_1 + \omega_2 E_2 + \omega_3 E_3)$, $\omega_1, \omega_2, \omega_3 \in \mathbb{R}$, so that the new acidic and base components vanish:

$$\exp(\omega_1 E_1 + \omega_2 E_2 + \omega_3 E_3) \begin{pmatrix} \sqrt{\gamma_0^{LW}} \\ \sqrt{\gamma_0^+} \\ \sqrt{\gamma_0^-} \end{pmatrix} = \begin{pmatrix} \sqrt{\gamma_0^{LW} + 2\sqrt{\gamma_0^+} \sqrt{\gamma_0^-}} \\ 0 \\ 0 \end{pmatrix} . \quad (2.13)$$

As explicitly written in the previous equation, the new dispersive component must be set to $\gamma_0^{LW} + 2\sqrt{\gamma_0^+} \sqrt{\gamma_0^-}$, owing to the invariance of $\gamma^{LW} + 2\sqrt{\gamma^+} \sqrt{\gamma^-}$. Condition (2.13) is equivalent to

$$\frac{1}{\sqrt{\gamma_0^{LW} + 2\sqrt{\gamma_0^+} \sqrt{\gamma_0^-}}} \begin{pmatrix} \sqrt{\gamma_0^{LW}} \\ \sqrt{\gamma_0^+} \\ \sqrt{\gamma_0^-} \end{pmatrix} = \exp(-\omega_1 E_1 - \omega_2 E_2 - \omega_3 E_3) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \quad (2.14)$$

$$= \begin{pmatrix} \text{Ch}R - \omega_3^2 \frac{\text{Ch}R - 1}{R^2} \\ \omega_2 \left(\frac{\text{Sh}R}{R} - \omega_3 \frac{\text{Ch}R - 1}{R^2} \right) \\ \omega_1 \left(\frac{\text{Sh}R}{R} + \omega_3 \frac{\text{Ch}R - 1}{R^2} \right) \end{pmatrix} \equiv \begin{pmatrix} \rho \\ \sigma \\ \tau \end{pmatrix}, \quad \text{with } R \equiv \sqrt{\omega_3^2 - 2\omega_1\omega_2} \in \mathbb{R} \cup i\mathbb{R}$$

and $\text{Ch}R = (e^R + e^{-R})/2$, $\text{Sh}R = (e^R - e^{-R})/2 \forall R \in \mathbb{C}$. We have to show that any vector $(\rho \ \sigma \ \tau)^T$ satisfying $\rho, \tau, \sigma \geq 0$ and $\rho^2 + 2\sigma\tau = 1$ can be obtained from (2.14) for a suitable choice of $\omega_1, \omega_2, \omega_3 \in \mathbb{R}$. Actually, it can be proved even more: that the following map

$$(\omega_1, \omega_2, \omega_3) \in \{(x_1, x_2, x_3) \in \mathbb{R}^3 : x_3^2 - 2x_1x_2 \geq 0\} \longrightarrow$$

$$\begin{pmatrix} \text{Ch}R - \omega_3^2 \frac{\text{Ch}R - 1}{R^2} \\ \omega_2 \left(\frac{\text{Sh}R}{R} - \omega_3 \frac{\text{Ch}R - 1}{R^2} \right) \\ \omega_1 \left(\frac{\text{Sh}R}{R} + \omega_3 \frac{\text{Ch}R - 1}{R^2} \right) \end{pmatrix} \in \left\{ \begin{pmatrix} \rho \\ \sigma \\ \tau \end{pmatrix} : \rho^2 + 2\sigma\tau = 1, \rho, \sigma, \tau \in \mathbb{R} \right\}$$

is onto — although not one-to-one. Therefore, we can confine ourselves to consider $R \geq 0$ and the entire functions $\text{Ch}R$, $(\text{Ch}R - 1)/R^2$, $\text{Sh}R/R$ will never vanish. Our first goal is to choose R and ω_3 in such a way that $\rho = \rho_0$, any preassigned real value. We preliminary take R in such a way that $\text{Ch}R > \rho_0$ and then we determine an $\omega_3 \in \mathbb{R}$ which satisfies

$$\text{Ch}R - \omega_3^2 \frac{\text{Ch}R - 1}{R^2} = \rho_0.$$

Existence of the above ω_3 — and its uniqueness up to a change of sign — is obvious since both $\text{Ch}R$ and $(\text{Ch}R - 1)/R^2$ are strictly positive. The product $\omega_1\omega_2$ is now uniquely fixed and for the components σ, τ we have $\sigma\tau = (1 - \rho_0^2)/2$. A very tedious but rather simple algebraic calculation shows that the parameters ω_1, ω_2 , can be always chosen in such a way that $(\sigma, \tau) = (\sigma_0, \tau_0)$ for any given (σ_0, τ_0) satisfying $\sigma_0\tau_0 = (1 - \rho_0^2)/2$.

This remark implies that Theorem 3 can be put in a stronger — although not particularly useful, as a rule — form, by extending the validity of (2.6) also to the case $\xi = 1$.

The previous result gives us the possibility of assigning the vOCG components of a particular liquid almost arbitrarily. A natural question is whether after this assignment a certain amount of indeterminacy is still available. An investigation of the spectral properties of matrices in \mathbb{G}_3 provides a satisfactory answer to the problem.

Theorem 4

Let $C \in \mathbb{G}_3$. Then:

(i) there holds $\det(C - \lambda\mathbb{I}) = \det(C^{-1} - \lambda\mathbb{I})$, so that if λ is an eigenvalue, λ^{-1} also is.

The spectrum of C always includes $+1$ or -1 ;

(ii) the eigenvalues of $C = \exp(\omega_1 E_1 + \omega_2 E_2 + \omega_3 E_3)$, $\omega_1, \omega_2, \omega_3 \in \mathbb{C}$, are

$$1 \quad e^{\sqrt{\omega_3^2 - 2\omega_1\omega_2}} \quad e^{-\sqrt{\omega_3^2 - 2\omega_1\omega_2}}$$

for $\omega_3^2 - 2\omega_1\omega_2 \neq 0$, whereas in the opposite case there is a unique eigenvalue $+1$ with geometric multiplicity 1. In any case, for $(\omega_1, \omega_2, \omega_3) \neq (0, 0, 0)$ the eigenspace of $+1$ — kernel of $C - \mathbb{I}$ — coincides with the following set

$$\text{Ker}(C - \mathbb{I}) = \{ \mu(\omega_3 \ \omega_2 \ -\omega_1)^T, \ \mu \in \mathbb{C} \setminus \{0\} \} .$$

Proof

From the definition of \mathbb{G}_3 we have that $C^T R = RC^{-1}$ and therefore

$$C^T R - \lambda R = RC^{-1} - \lambda R \quad \iff \quad (C^T - \lambda\mathbb{I})R = R(C^{-1} - \lambda\mathbb{I}) ,$$

which implies

$$\det(C^T - \lambda\mathbb{I}) \det R = \det R \det(C^{-1} - \lambda\mathbb{I}) \quad \iff \quad \det(C^T - \lambda\mathbb{I}) = \det(C^{-1} - \lambda\mathbb{I})$$

so that C and C^{-1} have the same characteristic polynomial of order three. This proves item (i). As for item (ii), we preliminary observe that if $(x_1 \ x_2 \ x_3)^T$ is an eigenvector

of $E = \omega_1 E_1 + \omega_2 E_2 + \omega_3 E_3$ with eigenvalue λ , then the same $(x_1 \ x_2 \ x_3)^T$ provides an eigenvector of $\exp E$ with eigenvalue e^λ :

$$\exp E \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \sum_{n=0}^{\infty} \frac{1}{n!} E^n \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = e^\lambda \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}.$$

The spectrum of E is readily determined by means of the characteristic equation

$$\det(E - \mu \mathbb{I}) = \det \begin{vmatrix} -\mu & \omega_1 & \omega_2 \\ -\omega_2 & \omega_3 - \mu & 0 \\ -\omega_1 & 0 & -\omega_3 - \mu \end{vmatrix} = -\mu^3 + \mu(\omega_3^2 - 2\omega_1\omega_2) = 0$$

which provides $\mu = 0$, $+\sqrt{\omega_3^2 - 2\omega_1\omega_2}$, $-\sqrt{\omega_3^2 - 2\omega_1\omega_2}$. Consequently, whenever $\omega_3^2 - 2\omega_1\omega_2 \neq 0$ the matrix $\exp(E)$ admits three simple eigenvalues:

$$1 \quad e^{+\sqrt{\omega_3^2 - 2\omega_1\omega_2}} \quad e^{-\sqrt{\omega_3^2 - 2\omega_1\omega_2}}$$

and the eigenspace $\text{Ker}[\exp(E) - \mathbb{I}] = \text{Ker}(E)$ is specified by the nontrivial solutions $(x_1 \ x_2 \ x_3)^T$ of

$$0 = \begin{pmatrix} 0 & \omega_1 & \omega_2 \\ -\omega_2 & \omega_3 & 0 \\ -\omega_1 & 0 & -\omega_3 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \iff \begin{cases} +\omega_1 x_2 + \omega_2 x_3 = 0 \\ -\omega_2 x_1 + \omega_3 x_2 = 0 \\ -\omega_1 x_1 - \omega_3 x_3 = 0 \end{cases}$$

that is by $(x_1 \ x_2 \ x_3)^T = t(\omega_3 \omega_2 - \omega_1)^T$, $t \in \mathbb{C} \setminus \{0\}$. In the case $\omega_3^2 - 2\omega_1\omega_2 = 0$ the only eigenvalue of E is 0, with geometric multiplicity 1. The matrix can be then put into the Jordan form

$$E = Q^{-1} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} Q$$

in terms of an appropriate nonsingular 3×3 matrix Q . We deduce the expression for the exponential

$$\begin{aligned} \exp(E) &= Q^{-1} \sum_{n=0}^{\infty} \frac{1}{n!} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}^n Q = Q^{-1} \left[\mathbb{I} + \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \right] Q = \\ &= Q^{-1} \begin{pmatrix} 1 & 1 & 1/2 \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{pmatrix} Q \equiv Q^{-1} T Q, \quad T \equiv \begin{pmatrix} 1 & 1 & 1/2 \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{pmatrix}, \end{aligned}$$

whose eigenvectors coincide with those of the triangular matrix T , up to the transformation Q . The eigenspace $\text{Ker}T - \mathbb{I}$ is easily obtained from

$$0 = \begin{pmatrix} 0 & 1 & 1/2 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} x_2 + x_3/2 \\ x_3 \\ 0 \end{pmatrix} \implies \begin{matrix} x_2 = 0 \\ x_3 = 0 \end{matrix}$$

and we conclude that the geometric multiplicity of the only eigenvalue $+1$ is also 1. The eigenspace $\text{Ker}[\exp(E) - \mathbb{I}]$ is therefore the same obtained in the previous case. \square

An immediate consequence of Theorem 4 is the corollary below.

Corollary 4.1

A nonzero vector $(x_1 \ x_2 \ x_3)^T \in \mathbb{C}^3$ is invariant through the linear transformation defined by $C = \exp(\omega_1 E_1 + \omega_2 E_2 + \omega_3 E_3)$, $(\omega_1, \omega_2, \omega_3) \in \mathbb{C}^3 \setminus \{(0, 0, 0)\}$, if and only if

$$C = \exp[\mu(-x_3 E_1 + x_2 E_2 + x_1 E_3)]$$

for some $\mu \in \mathbb{C} \setminus \{0\}$. \square

3. Determination of scales in vOCG theory

We are now ready to apply the previous results to the problem of scale definition in vOCG theory. Suppose that the acid-base components $\gamma_{1,0}^{LW}$, $\gamma_{1,0}^+$, $\gamma_{1,0}^-$ of a material — referred to as “primary” reference chemical, from now on — have been estimated in some way. Under the general assumption that $\gamma_0^{LW} + 2\sqrt{\gamma_0^+ \gamma_0^-} > 0$, we can use Theorem 3 to redefine the components according to

$$\begin{aligned} \gamma_1^{LW} &= [\gamma_{1,0}^{LW} + 2\sqrt{\gamma_{1,0}^+} \sqrt{\gamma_{1,0}^-}] \xi \\ \gamma_1^+ &= [\gamma_{1,0}^{LW} + 2\sqrt{\gamma_{1,0}^+} \sqrt{\gamma_{1,0}^-}] \frac{1-\xi}{2} e^\eta \\ \gamma_1^- &= [\gamma_{1,0}^{LW} + 2\sqrt{\gamma_{1,0}^+} \sqrt{\gamma_{1,0}^-}] \frac{1-\xi}{2} e^{-\eta} \end{aligned} \tag{3.1}$$

with $\xi \in [0, 1)$ and $\eta \in \mathbb{R}$ arbitrarily chosen. By applying the linear transformation (3.1) to all the chemicals of the set, we get a preliminary definition of the acid-base scale. Such a definition is obviously not yet complete, since Corollary 4.1 states that there exists a one-parameter group of linear transformations $\mathbb{C}^3 \rightarrow \mathbb{C}^3$:

$$S(\mu) : \begin{pmatrix} \sqrt{\gamma^{LW}} \\ \sqrt{\gamma^+} \\ \sqrt{\gamma^-} \end{pmatrix} \longrightarrow \exp \left[\mu \left(-\sqrt{\gamma_1^-} E_1 + \sqrt{\gamma_1^+} E_2 + \sqrt{\gamma_1^{LW}} E_3 \right) \right] \begin{pmatrix} \sqrt{\gamma^{LW}} \\ \sqrt{\gamma^+} \\ \sqrt{\gamma^-} \end{pmatrix}, \quad (3.2)$$

with $\mu \in \mathbb{C}$, through which $(\sqrt{\gamma_1^{LW}} \sqrt{\gamma_1^+} \sqrt{\gamma_1^-})^T$ is invariant.

If $\gamma_{2,0}^{LW}, \gamma_{2,0}^+, \gamma_{2,0}^-$ are now the components of another material — the “secondary” reference chemical —, the linear transformation (3.2) allows us to write

$$\begin{pmatrix} \sqrt{\gamma_{2,0}^{LW}} \\ \sqrt{\gamma_{2,0}^+} \\ \sqrt{\gamma_{2,0}^-} \end{pmatrix} = \exp \left[\mu \left(-\sqrt{\gamma_1^-} E_1 + \sqrt{\gamma_1^+} E_2 + \sqrt{\gamma_1^{LW}} E_3 \right) \right] \begin{pmatrix} \sqrt{\gamma_{2,0}^{LW}} \\ \sqrt{\gamma_{2,0}^+} \\ \sqrt{\gamma_{2,0}^-} \end{pmatrix}$$

in such a way that the residual parameter μ can be possibly fixed by assigning one of the numbers $\sqrt{\gamma_{2,0}^{LW}}, \sqrt{\gamma_{2,0}^+}$ or $\sqrt{\gamma_{2,0}^-}$. The choice is not arbitrary, since:

- (a) the vectors $(\sqrt{\gamma_1^{LW}}, \sqrt{\gamma_1^+}, \sqrt{\gamma_1^-})$ and $(\sqrt{\gamma_{2,0}^{LW}}, \sqrt{\gamma_{2,0}^+}, \sqrt{\gamma_{2,0}^-})$ must be linearly independent, otherwise

$$(\sqrt{\gamma_{2,0}^{LW}}, \sqrt{\gamma_{2,0}^+}, \sqrt{\gamma_{2,0}^-}) \in \text{Ker} \left[\exp \left[\mu \left(-\sqrt{\gamma_1^-} E_1 + \sqrt{\gamma_1^+} E_2 + \sqrt{\gamma_1^{LW}} E_3 \right) \right] - \mathbb{I} \right]$$

and therefore

$$\begin{pmatrix} \sqrt{\gamma_{2,0}^{LW}} \\ \sqrt{\gamma_{2,0}^+} \\ \sqrt{\gamma_{2,0}^-} \end{pmatrix} = \exp \left[\mu \left(-\sqrt{\gamma_1^-} E_1 + \sqrt{\gamma_1^+} E_2 + \sqrt{\gamma_1^{LW}} E_3 \right) \right] \begin{pmatrix} \sqrt{\gamma_{2,0}^{LW}} \\ \sqrt{\gamma_{2,0}^+} \\ \sqrt{\gamma_{2,0}^-} \end{pmatrix} = \begin{pmatrix} \sqrt{\gamma_{2,0}^{LW}} \\ \sqrt{\gamma_{2,0}^+} \\ \sqrt{\gamma_{2,0}^-} \end{pmatrix}$$

$\forall \mu \in \mathbb{C}$. Components $\gamma_{2,0}^{LW}, \gamma_{2,0}^+, \gamma_{2,0}^-$ do not depend on μ and no full definition of the scale is possible;

(b) the transformation $S(\mu)$ can be explicitly written as

$$\begin{aligned}\sqrt{\gamma_2^{LW}} &= C_{11}\sqrt{\gamma_{2,0}^{LW}} + C_{12}\sqrt{\gamma_{2,0}^+} + C_{13}\sqrt{\gamma_{2,0}^-} \\ \sqrt{\gamma_2^+} &= C_{21}\sqrt{\gamma_{2,0}^{LW}} + C_{22}\sqrt{\gamma_{2,0}^+} + C_{23}\sqrt{\gamma_{2,0}^-} \\ \sqrt{\gamma_2^-} &= C_{31}\sqrt{\gamma_{2,0}^{LW}} + C_{32}\sqrt{\gamma_{2,0}^+} + C_{33}\sqrt{\gamma_{2,0}^-}\end{aligned}$$

with

$$\begin{aligned}C_{11} &= \text{Ch}(\mu r) - \gamma_1^{LW} \frac{\text{Ch}(\mu r) - 1}{r^2} \\ C_{12} &= -\sqrt{\gamma_1^-} \sqrt{\gamma_1^{LW}} \frac{\text{Ch}(\mu r) - 1}{r^2} - \sqrt{\gamma_1^-} \frac{\text{Sh}(\mu r)}{r} \\ C_{13} &= \sqrt{\gamma_1^+} \frac{\text{Sh}(\mu r)}{r} - \sqrt{\gamma_1^+} \sqrt{\gamma_1^{LW}} \frac{\text{Ch}(\mu r) - 1}{r^2} \\ C_{21} &= -\sqrt{\gamma_1^+} \frac{\text{Sh}(\mu r)}{r} - \sqrt{\gamma_1^+} \sqrt{\gamma_1^{LW}} \frac{\text{Ch}(\mu r) - 1}{r^2} \\ C_{22} &= \text{Ch}(\mu r) - \sqrt{\gamma_1^-} \sqrt{\gamma_1^+} \frac{\text{Ch}(\mu r) - 1}{r^2} + \sqrt{\gamma_1^{LW}} \frac{\text{Sh}(\mu r)}{r} \\ C_{23} &= -\gamma_1^+ \frac{\text{Ch}(\mu r) - 1}{r^2} \\ C_{31} &= -\sqrt{\gamma_1^-} \sqrt{\gamma_1^{LW}} \frac{\text{Ch}(\mu r) - 1}{r^2} + \sqrt{\gamma_1^-} \frac{\text{Sh}(\mu r)}{r} \\ C_{32} &= -\gamma_1^- \frac{\text{Ch}(\mu r) - 1}{r^2} \\ C_{33} &= -\sqrt{\gamma_1^-} \sqrt{\gamma_1^+} \frac{\text{Ch}(\mu r) - 1}{r^2} + \text{Ch}(\mu r) - \sqrt{\gamma_1^{LW}} \frac{\text{Sh}(\mu r)}{r}\end{aligned}$$

and $r = \sqrt{\gamma_1^{LW} + 2\sqrt{\gamma_1^+ \gamma_1^-}}$. All the square roots of the new components are given by expressions of the form

$$a + be^{\mu r} + ce^{-\mu r}$$

for suitable constants a, b, c dependent on $\gamma_{2,0}^{LW}, \gamma_{2,0}^+, \gamma_{2,0}^-, \gamma_1^{LW}, \gamma_1^+, \gamma_1^-$ and on the component. Constraints on the admissible values of $\mu \in \mathbb{C}$ come from the requirement that each $\sqrt{\gamma_2^{LW}}, \sqrt{\gamma_2^+}, \sqrt{\gamma_2^-}$ be real and nonnegative. Typically, μ will belong to some real interval.

We expect that whenever the secondary reference chemical is chosen appropriately, so as to accomplish conditions (a) and (b) for some μ , the parameter takes a uniquely determined

value $\mu = \mu^*$ by assigning one of the components γ_2^{LW} , γ_2^+ , γ_2^- . A mapping through $S(\mu^*)$ of the whole component set will provide the requested scale.

It is noticeable that the self-consistency of the method imposes all the square roots of the final components to be nonnegative, thus not any choice will yield satisfactory results. In this sense, both primary and secondary reference material must be selected “judiciously”, and the conventional values of the corresponding components assigned in a proper way.

4. Quadratic multicomponent theories

In the late 60s a prototype of multicomponent theory was already proposed by Owens and Wendt^[10] (OW), in order to determine the specific contribution of dispersive and “polar” interactions to the whole work of adhesion. This is accomplished by the definition of suitable dispersive and polar contributions for each material, in such a way that

$$\gamma_l = \gamma_l^d + \gamma_l^p \quad \gamma_s = \gamma_s^d + \gamma_s^p$$

for liquids and solids respectively. The work of adhesion becomes, accordingly,

$$W^{\text{adh}} = 2 \left[\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} \right],$$

a sort of geometric-mean rule being separately applied to dispersive and polar components. The theory can be easily extended, for instance to take specifically into account hydrogen-bonding interactions

$$\gamma_l = \gamma_l^d + \gamma_l^p + \gamma_l^H \quad \gamma_s = \gamma_s^d + \gamma_s^p + \gamma_s^H$$

$$W^{\text{adh}} = 2 \left[\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} + \sqrt{\gamma_s^H \gamma_l^H} \right]$$

by introducing further appropriate components, labelled by H . A recent revision of vOCG theory led Qin and Chang^[11-13] (QC) to propose a new, in principle more general three-parameter model whose equations reduce to

$$\gamma_l = \frac{1}{2}(P_l^d)^2 - P_l^a P_l^b \quad \gamma_s = \frac{1}{2}(P_s^d)^2 - P_s^a P_s^b$$

$$W^{\text{adh}} = P_s^d P_l^d - (P_s^a P_l^b + P_s^b P_l^a),$$

the superscripts d , a and b corresponding to LW -dispersive, Lewis-acidic and Lewis-basic components respectively. Although not developed to predict adhesion work or surface free energy, other models show a very similar structure. A well-known example is Drago's theory^[14-16] which distinguishes "acidic" and "basic" solvents (electron acceptors and donors) and writes the enthalpy of adduct formation for any acceptor-donor pair as

$$-\Delta H = C_A C_B + E_A E_B$$

where the subscripts A and B indicate acceptor and donor and E and C represent electrostatic and covalent contributions. Analogous empirical two-parameters relationships for free energy have also been established by electrochemical techniques by Edwards^[17], Mulliken^[18] and Foss^[19]. Drago's theory may be readily extended to take into account the eventual co-existence of acidic and basic sites in the same molecule by an equation of the form^[20]

$$-\Delta H = C_A C'_B + C_B C'_A + E_A E'_B + E_B E'_A. \quad (4.1)$$

In recent papers^[7,21] it has been recognized that from a mathematical point of view the GvOC theory should be classified in the realm of Linear Free Energy or Solvation Energy Relationships (LFER or LSER)^[22,23], where a thermodynamical quantity Q , pertaining in this case to Lewis acid-base properties of two materials X and Y, is expressed as a sum of pairwise products of some material coefficients

$$Q = \sum_i X_i Y_i.$$

The index i refers to the class of the coefficient: dispersive, acidic, basic and so forth, while symbols X and Y pertain to the interacting materials. Such a kind of relations is widely applied in physical organic chemistry^[22,23]. All the above multicomponent models involve *bilinear and quadratic forms* of components, for adhesion work and surface free

energy respectively: they will be called Quadratic Multicomponent Models. Not all the multicomponent theories have the same structure; an interesting counterexample is the model by Wu^[24,25], who distinguishes dispersive and “polar” contributions to adhesion work, as in WO, but adopting a harmonic-mean combining rule instead of a geometric-mean approximation

$$W^{\text{adh}} = 4 \left[\frac{\gamma_l^d \gamma_s^d}{\gamma_l^d + \gamma_s^d} + \frac{\gamma_l^p \gamma_s^p}{\gamma_l^p + \gamma_s^p} \right].$$

The general mathematical form of quadratic multicomponent models is immediately recognized. The model equations appear to be the same of vOCG theory in matrix notation

$$\gamma_l = X^T R X \quad \gamma_s = Y^T R Y \quad W^{\text{adh}} = 2X^T R Y \quad (4.2)$$

or the only third equation as in the case of Drago’s theory, depending on whether it does make sense to consider or it is of interest to model interactions of a material with itself (in theories like vOCG, QC or OW, self-interaction describes surface free energy or surface tension). Now, however, X and Y denote c -dimensional column vectors of material components (e.g. for each liquid and solid) or quantities simply related to them (square roots of components, suitably scaled components, etc.), while R is any real, symmetrical nonsingular $c \times c$ “structure” matrix characteristic of the model. If d_1, \dots, d_c denote the (real and nonvanishing) eigenvalues of R and $\text{sgn}(x)$ the sign function, by an appropriate linear transformation of vectors X and Y it is always possible to reduce the structure matrix to the standard form

$$R = \begin{pmatrix} \text{sgn}(d_1) & & \mathbb{O} \\ & \ddots & \\ \mathbb{O} & & \text{sgn}(d_c) \end{pmatrix}.$$

Multicomponent models of the form (4.2) are thus properly different only if their structure matrices do not share the same signature $\{\text{sgn}(d_1), \dots, \text{sgn}(d_c)\}$, otherwise they should be regarded as mathematically equivalent up to a linear redefinition of components^[20] — i.e. up to an isomorphism.

5. Scale definition in quadratic multicomponent theories

In a way similar to the proof of Theorem 1 it is easy to check that the model equations (4.2) are invariant through any linear transformation $X \rightarrow CX$, $Y \rightarrow CY$, whenever the real matrix C satisfies $C^T RC = R$. The set of matrices C

$$\mathbb{G} = \{C \text{ real } c \times c \text{ nonsingular matrix} : C^T RC = R\} \quad (5.1)$$

forms a nonabelian group with respect to the common product, since $\mathbb{I}^T R \mathbb{I} = R$, while $C^T RC = C$ implies $(C^{-1})^T RC^{-1} = R$ and finally

$$C^T RC = R, \quad D^T RD = R \quad \implies \quad (CD)^T RCD = D^T C^T RCD = D^T RD = R.$$

As in the case of vOCG theory, scale multiplicity due to the invariance transformation group (5.1) has the important consequence that the material parameters (components) of a quadratic multicomponent model do not necessarily admit a direct interpretation, unless they are susceptible of a direct measurement. Due to the “extrathermodynamical” character of material components, such a constraint is quite typical. As an example, vOCG acid-base components are calculated *only* by surface tension and contact angle data, solving the same model equations of the theory, and cannot be estimated in a direct way. The unique alternative would be to establish a correspondence of a suitable vOCG scale with some other scales of acid-base strength admitting a direct measurement of model parameters, a correspondence which is missing at the present state of the art.

One can also immediately prove that matrices $C \in \mathbb{G}$ have very special spectral properties, since if $\lambda \in \mathbb{C}$ is an eigenvalue of C , so is λ^{-1} . Matrices $C \in \mathbb{G}$ may also be interpreted as describing changes of bases in the linear space \mathbb{R}^c endowed with a bilinear symmetric metric of matrix representation R , provided that the change of bases preserves the metric. \mathbb{G} can then be visualized as a metric-preserving group and identified with the (generalized)

orthogonal group $O(c_+, c_-; \mathbb{R})$, on having denoted with c_+ and c_- the number of positive and negative eigenvalues of R , respectively^[26]. Once again, we have a confirmation that the multicomponent model and its invariance group of transformations depend uniquely on the signature of the structure matrix R . In this respect, it is worthy of note that interchanging c_+ with c_- is equivalent to replacing the metric by its negative and thus gives the same group.

As an analytic manifold the group $O(c_+, c_-; \mathbb{R})$ has dimension $c(c-1)/2$, with $c = c_+ + c_-$. This means that locally the elements of the group are completely specified by $c(c-1)/2$ real parameters through an analytical parametrization defined in a suitable neighborhood of 0 in $\mathbb{R}^{c(c-1)/2}$. From a topological point of view this Lie group is not connected, consisting of 4 connected topological components, but it is always possible — and physically reasonable — to confine ourselves to the only connected component containing the unity, that is the $c \times c$ unit matrix \mathbb{I} . Such a choice seems anyway satisfactory, since the connected topological component containing unity constitutes a subgroup^[26], often denoted as $SO^+(c_+, c_-; \mathbb{R})$. The structure of the group in a neighborhood of unity can be detailed described in an elementary way. Indeed any matrix close to unity can be written into the form

$$\mathbb{I} + \epsilon D + o(\epsilon) \quad (\epsilon \rightarrow 0) \tag{5.2}$$

in terms of the scalar $\epsilon \in \mathbb{R}$ and of any $c \times c$ real matrix D satisfying

$$[\mathbb{I} + \epsilon D^T + o(\epsilon)] R [\mathbb{I} + \epsilon D + o(\epsilon)] = R \quad (\epsilon \rightarrow 0)$$

or, equivalently,

$$RD + D^T R = 0. \tag{5.3}$$

By using the symmetry of the structure matrix R , equation (5.3) reduces to

$$RD + (RD)^T = 0$$

and therefore the most general form of D must be

$$D = R^{-1}\Omega \tag{5.4}$$

on having denoted with Ω any real skewsymmetric $c \times c$ matrix, which depends on $c(c-1)/2$ parameters. Vice versa, a simple calculation shows that whenever (5.3) is satisfied the exponential of D

$$\exp(D) = \sum_{n=0}^{\infty} \frac{1}{n!} D^n = \lim_{n \rightarrow +\infty} \left(\mathbb{I} + \frac{D}{n} \right)^n$$

belongs to \mathbb{G} . Matrices in the connected component of \mathbb{G} containing \mathbb{I} can be expressed as exponentials of some generator D and used to chose scales.

In order to remove multiplicity and specify a unique well-defined scale, a conventional assignment of component values to some reference compounds is needed. The most general matrix $C \in \mathbb{G}$ is completely determined by $c(c-1)/2$ parameters, thus the reference components must be chosen accordingly. Selection of a scale for a specific quadratic multicomponent model requires a detailed analysis, similar to that previously illustrated for vOCG theory. Nevertheless the general strategy does not change in an appreciable way when the group $O(2, 1; \mathbb{R})$ involved in vOCG analysis is replaced by a generic $O(c_+, c_-; \mathbb{R})$. For instance, the selection of component scales for the extended Drago model (4.1) can be accomplished by transformation matrices of the form

$$C = \exp \begin{pmatrix} -\omega_1 & 0 & \omega_4 & \omega_5 \\ 0 & \omega_1 & \omega_2 & \omega_3 \\ -\omega_4 & -\omega_5 & -\omega_6 & 0 \\ -\omega_2 & -\omega_1 & 0 & \omega_6 \end{pmatrix} \quad \forall \omega_i \in \mathbb{R}, \quad i = 1, 2, \dots, 6$$

obtained from (5.4) by the idempotent structure matrix

$$R = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

and the most general 4×4 skew-symmetric matrix Ω . The most important consequence is that, since the dimensionality of the invariance group involved does not depend on the detailed signature of the model structure matrix, the number of material components which is necessary to assign in order to select a specific scale is typically related only to the number c of components per material assumed by the theory.

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