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BRIEF COMMUNICATION

New Acid Sites in Dilute Oxide Solid Solutions: An Optical Basicity Approach

J. H. BINKS AND J. A. DUFFY

Chemistry Department, The University, Old Aberdeen AB9 2UE, Scotland

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Optical basicity values are obtained for groups in dilute oxide solid solutions, where protons compensate for lower oxidation state cations substituting for cations of the host oxide. These values are compared with the optical basicity of the host oxide. The results are discussed in the context of current models.

It is well known that mixing certain binary oxides, to produce dilute solid solutions, results in the formation of new acid sites (*1*). Simple electrostatic models have been proposed to explain this effect and their worth has been proved by the success of their correlation and prediction (*2, 3*). Explanations have also been presented in terms of a quantum-chemical approach designed to calculate, among other parameters, the energy necessary for proton removal from the site (*4*).

We should like to approach the problem from the point of view of the optical basicity concept (*5*), since not only does this theory embrace features from both the electrostatic model and electron density calculations, but also it gives an insight into an interesting aspect, raised recently by Kung (*3*), concerning the location of the new acid site. Kung's model has indicated for a dilute solid solution obtained by dissolving an oxide AO_y into the host BO_z, such that a small amount of A^{2y+} ions are substituted in the B^{2z+} sites, that the new acidic sites are formed (i) at the substituting cation site, or (ii) on the matrix surface far away from the substitution site. Kung explains how the sites can be generated, and for the case where the substituting cation has a lower oxidation number than the cation of the oxide (the case we shall consider here), the acidity is presumed to be due to the presence of protons that compensate for the difference in cation oxidation number. The chemical groups constituting the two types of site are distinct and can be formulated as (i) $B_nAH_{2z-2y}O_{(n+1)z}$ (acidity at the substituted site), and (ii) $B_nH_{2z-2y}O_{(n+1)z-y}$ (acidity remote from the sphere of influence of A^{2y+}).

There is much evidence, spectroscopic and quantum-chemical (*6, 7*), that the optical basicity, Λ, of an oxidic system is proportional to the average electron density on the oxygens. Λ can be calculated from

$$\Lambda = X_A\Lambda(AO_y) + X_B\Lambda(BO_z) + \dots \quad (1)$$

where X_A, X_B, . . . , are the equivalent fractions of the cations A^{2y+}, B^{2z+}, . . . ,

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relative to the total number of oxide ions, and $\Lambda(AO_y)$, $\Lambda(BO_z)$, . . . , are the optical basicities of the binary oxides (see Table I). It is reasonable to assume that if either of the two chemical groups, (i) and (ii) above, acts as a newly acidic site, then its oxygen electron density, that is, its Λ value, will be less than for the original host oxide BO_z. (Correlation of Λ of oxyanions with pK_a values of oxyacids supports this idea (5).) Using Eq. (1) the Λ values of the two groups are as follows:

$$\Lambda(B_nAH_{2z-2y}O_{(n+1)z}) = \frac{nz}{(n+1)z}\Lambda(BO_z) + \frac{y}{(n+1)z}\Lambda(AO_y) + \frac{z-y}{(n+1)z}\Lambda(H_2O) \quad (2)$$

$$\Lambda(B_nH_{2z-2y}O_{(n+1)z-y}) = \frac{nz}{(n+1)z-y}\Lambda(BO_z) + \frac{z-y}{(n+1)z-y}\Lambda(H_2O) \quad (3)$$

Inspecting Eq. (3) first, it is apparent that the Λ value will always be less than that of the host oxide BO_z, providing that (apart from the oxidation number of A being less than that of B) $\Lambda(BO_z)$ is greater than $\Lambda(H_2O)$ (see Appendix). In Table I, this is the case for all the metal oxides and boric oxide: the binary oxides having $\Lambda < \Lambda(H_2O)$ are those of nonmetallic elements and are molecular compounds. For "network" or ionic oxides, to which the present discussion applies, it follows that when protons take up positions to compensate for the oxidation number difference between A^{2y+} and B^{2z+}, but which are outside the sphere of direct influence of the cation A^{2y+}, the sites will always be acidic. Turning now to the Λ value for the sites where the cation A^{2y+} is involved (Eq. (2)), it can be shown (see Appendix) that this value is less than $\Lambda(BO_z)$ only when $\Lambda(AO_y)$ fulfills

$$\Lambda(AO_y) < \frac{z}{y}\Lambda(BO_z) - \frac{z-y}{y}\Lambda(H_2O). \quad (4)$$

TABLE I

Λ VALUES FOR BINARY OXIDES (5)

Oxide	Λ
Cl_2O_7	0.27
SO_3	0.33
P_2O_5	0.40
H_2O	0.40
B_2O_3	0.42
SiO_2	0.48
Al_2O_3	0.60
MgO	0.78
CaO	1.00
BaO	1.15
Na_2O	1.15
K_2O	1.4

Thus, if $\Lambda(AO_y)$ exceeds this value, a newly acidic site will not be formed at the substituting cation site, despite the presence of a proton.

If we take, as an example, the host oxide (BO_z) to be SiO_2 and consider reaction with an oxide of stoichiometry M_2O_3, then the critical Λ value for M_2O_3 is (Eq. (4)) $[2/1\frac{1}{2}]\Lambda(SiO_2) - [(4-3)/3]\Lambda(H_2O)$. With $\Lambda(SiO_2) = 0.48$ and $\Lambda(H_2O) = 0.40$ (Table I), this equals 0.51. Thus, if M_2O_3 is Al_2O_3, for which Λ is 0.61 (cf. $\Lambda(SiO_2) = 0.48$), the acidic site is formed outside the sphere of direct influence of the Al^{3+}. On the other hand, if M_2O_3 is B_2O_3, for which Λ is 0.42, then the site containing the B^{3+} ion can be responsible for the acidity.

The groups which have been formulated as (i) $B_nAH_{2z-2y}O_{(n+1)z}$ and (ii) $B_nH_{2z-2y}O_{(n+1)z-y}$ are somewhat notional since they do not exist as detached from the rest of the structure. The perturbing effects of A^{2y+} and H^+ ions on the B^{2z+}–O^{2-} interaction gradually decrease with distance, and therefore the value of n is indeterminate. Nevertheless, it is worthwhile to plot the trends in Λ, for the above species, with in-

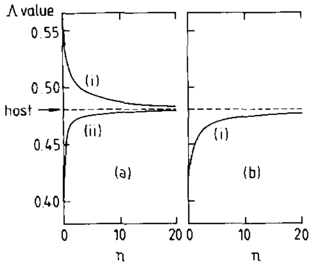

FIG. 1. Trends in Λ in the species (i) $B_nAH_{2z-2y}O_{(n+1)z}$ and (ii) $B_nH_{2z-2y}O_{(n+1)z-y}$ with increasing values of n (Eqs. (2) and (3)). In (a) $\Lambda(AO_y)$ is greater than $(z/y)\Lambda(BO_z) - ((z-y)/y)\Lambda(H_2O)$, and in (b) it is less. The scale of the ordinate is when BO_z is silica and AO_y is aluminum oxide (in (a)) or boric oxide (in (b)).

creasing n and these are shown in Fig. 1. The specific examples chosen are for the host SiO_2 and the substituting tripositive ions: (a) Al^{3+} and (b) B^{3+}.

It must be emphasized that in this treatment, the purpose of formulating the groups (i) and (ii) above is so that comparisons can be made with the original host oxide in accordance with the model previously proposed by Kung (*3*). It is not presumed that the groups themselves are responsible for the release of protons. Indeed, previous correlations between optical basicity and Hammett acidity function (*8*) suggest that an additional proton is present in the group to account for the acidities observed for these materials. Finally, it should be noted that the present treatment does not necessarily allow comparisons in acidity to be made for different systems; for example, it is not possible to compare the silica host materials SiO_2–Al_2O_3 and SiO_2–MgO with each other, since the groups of formula $Si_nHO_{2n+1/2}$ and Si_nO_{2n+1}, respectively generated, would almost certainly have different values of n.

Appendix

For $\Lambda(B_nH_{2z-2y}O_{(n+1)z-y})$ to be less than $\Lambda(BO_z)$,

$$\Lambda(B_nH_{2z-2y}O_{(n+1)z-y}) - \Lambda(BO_z) < \text{zero}.$$

From Eq. (3),

$$\frac{z-y}{(n+1)z-y}\Lambda(H_2O) - \frac{z-y}{(n+1)z-y}\Lambda(BO_z) < \text{zero},$$

i.e., $\Lambda(BO_z) > \Lambda(H_2O)$. For $\Lambda(B_nAH_{2z-2y}O_{(n+1)z})$ to be less than $\Lambda(BO_z)$,

$$\Lambda(B_nAH_{2z-2y}O_{(n+1)z-y}) - \Lambda(BO_z) < \text{zero}.$$

From Eq. (2),

$$\frac{y}{(n+1)z}\Lambda(AO_y) + \frac{z-y}{(n+1)z}\Lambda(H_2O) - \frac{z}{(n+1)z}\Lambda(BO_z) < \text{zero},$$

i.e., $\Lambda(AO_y) < (z/y)\Lambda(BO_z) - ((z-y)/y)\Lambda(H_2O)$.

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