

## Use of Donor Scales in selecting the Optimum Solvent for Complexation Reaction of Bi(III) and Sb(III) in Non-aqueous Medium.

N.T. YATSIMIRSKAYA AND RAFEE ARAIN

*Department of Analytical Chemistry, Moscow State University Moscow.*

(Received 28th January, 1980, Revised 20th December 1980)

**Summary:** Relative free energy of complex formation of bismuth(III) with Diphenyl diselenophosphate ion in gaseous phase has been calculated through extrathermodynamic method for the first time in solving the problem arising out of a complicated equilibrium with the participation of organic ligand having a complex structure. A new bi-parameter equation correlating stability constants with Donor and Acceptor number of the solvents has been proposed. This approach can provide sound basis in the selection of optimum solvents for use in Analytical Chemistry and several inorganic preparations. Some practical steps have been underlined.

### Introduction

Just the electrostatic considerations or for that matter the Dielectric constant of the medium are not sufficient to explain the effect of solvent on stability constant values. The main effect comes through the very nature of the solvent specially its donating ability or donor strength. A linear correlation between the stability constant values and Donor Number (DN-a measure of donor strength) has been established<sup>1</sup>.

In an earlier report<sup>2</sup> while discussing the quantitative effect of solvent donicity on stability constants it was found that the values of stability constants find a better correlation with donor scale based on the enthalpy of adduct formation with Iodine rather than with  $\text{DN}_{\text{SbCl}_5}$ . At this stage of developments in non-aqueous medium it is difficult to provide any theoretical base for such differentiations. It can nevertheless be attributed to some compensations in contributions made, due to interactions, to the overall complex formation energy, when we go from standard acceptor  $\text{SbCl}_5$  to  $\text{I}_2$ . Moreover these deviations indicate that along with solvent donicity a number of other factors affecting stability constants are to be considered. In this report an attempt has been made by considering the complexation of bismuth with potassium diphenyldiselenophosphate to give full accountability of these factors by referring to gas-phase energies of complexation. The introduction of Acceptor

Numbers<sup>1</sup> of the solvent gives a better correlation with physically more viable donor numbers.

### Discussions

Stability constant values of Bi(III) and Sb(III) with potassium diphenyldiselenophosphate (dsp) in various organic solvents are listed table 1. Figure 1 illustrates the dependence of logarithm of stability constants on donor number. It can be seen that generally a linear correlation is observed here while in figure 2 the deviation, in the correlation of logarithm of stability constants with the enthalpy of adduct formation with Iodine, is minimised. These deviations in correlation with donicity show that along with solvent donicity a number of factors affecting the stability constant values are to be considered.

In this connection lets consider the thermodynamic cycle (Eq. 1) illustrating a relation between standard free energy of Bi(III) complexes with dsp in solution and gaseous phase. Expression for free energy of reaction in gaseous phase is as under:

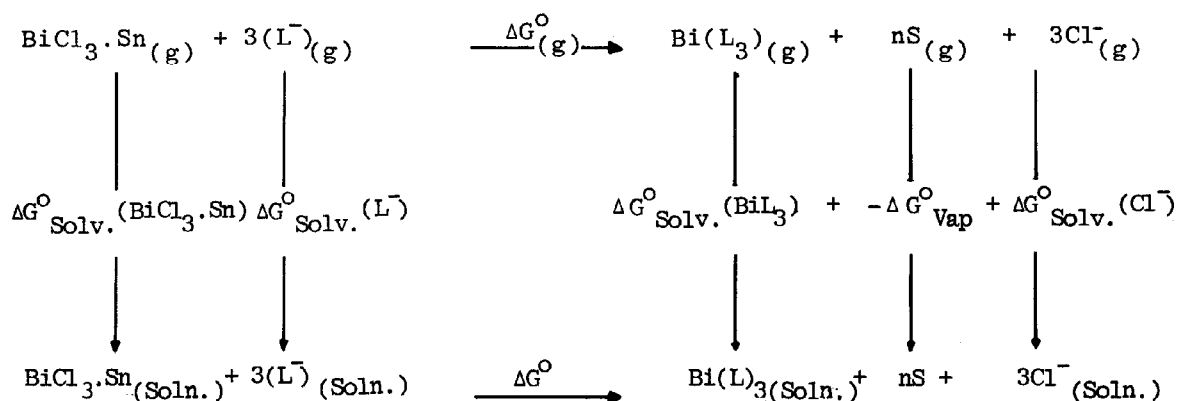
$$\Delta G_{(g)}^{\circ} = \Delta G^{\circ} + \Delta G_{\text{solv}}^{\circ}(\text{L}^-) + \Delta G^{\circ}(\text{BiCl}_3 \cdot \text{Sn}) + \Delta G_{\text{vap}}^{\circ} - \Delta G_{\text{solv}}^{\circ}(\text{BiL}_3) - \Delta G_{\text{solv}}^{\circ}(\text{Cl}^-) \quad (2)$$

Table 1

Stability constants of dsp complexes with Bi (III) and Sb (III), in some organic solvents.

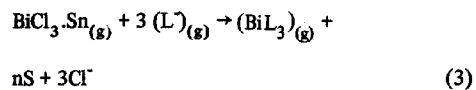
Solvent	Bi (III) $\beta_3, M^{-3}$	Sb (III) $\beta_3, M^{-3}$
MeCN	$(1.3 \pm 0.2)10^{13}$	
Me <sub>2</sub> CO	$(3.2 \pm 0.2)10^{10}$	$(2.5 \pm 0.2)10^{10}$
EtOH	$(2.5 \pm 0.3)10^{14}$	$(1.4 \pm 0.1)10^4$
TBF		$(6.5 \pm 0.2)10^9$
DMF	$(1.6 \pm 0.1)10^5$	
DMSO	$(1.7 \pm 0.1)10^2$	

data taken from reference 2.

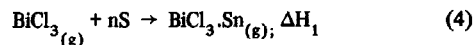
Thermodynamic Cycle (Equation 1)

where  $\Delta g^\circ_{(g)}$  and  $\Delta G^\circ$  - Standard free energy of complexation reaction in gas-phase and solution respectively (standard state 1 M solution);  $\Delta G^\circ_{\text{Solv.}}(\text{L}^-)$ ,  $\Delta G^\circ_{\text{Solv.}}(\text{BiCl}_3 \cdot \text{Sn})$ ,  $\Delta G^\circ_{\text{Solv.}}(\text{BiL}_3)$  and  $\Delta G^\circ_{\text{Solv.}}(\text{Cl}^-)$  - Standard free energy of solvation of dsp,  $\text{BiCl}_3 \cdot \text{Sn}$ , complex and chloride ion respectively;  $\Delta G^\circ_{\text{vap}}$  Standard free energy of vaporisation of solvent.

Thus the standard free energy of complexation in solvent consists of, energy of solvating species, energy of vaporization of solvent and free energy of reaction in gaseous phase. While  $\Delta G^\circ_{(g)}$  depends only on the donor properties of the solvent (S) molecules:



The above reaction can be presented through the following process:



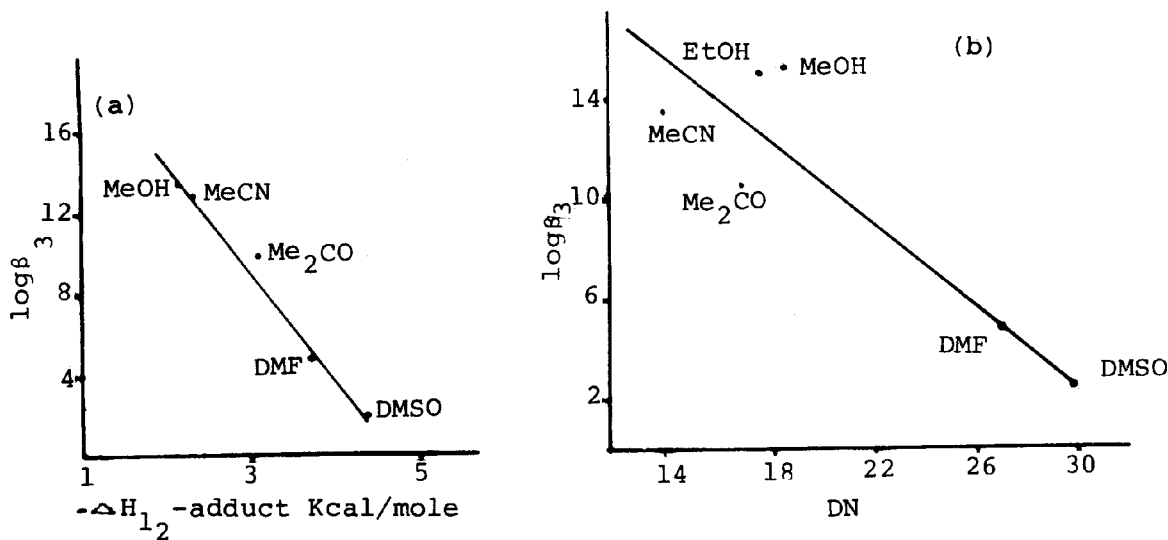


Fig. 1. Dependence of  $\log \beta_3$  on (a)  $-\Delta H_{1_2}$ -adduct formation of the solvent with iodine and (b) DN of the solvent; for the complexation of Bi(III) with dsp.

from where  $\Delta H_1$  should be proportional to the donicity of the solvent molecules:

$$\Delta H_1 = f DN_{SbCl_5} \quad (6)$$

where  $f$  – is the measure of accepting capability of  $BiCl_3$  with respect to  $SbCl_5$ .

Standard free enthalpy of (3) is equal to:

$$\Delta H^\circ_{(g)} = \Delta H_1 + \Delta H_2 \quad (7)$$

and subsequently;

$$\Delta G^\circ_{(g)} = f DN_{SbCl_5} + \Delta H_2 - T \Delta S^\circ_{(g)} \quad (8)$$

Since the entropy change  $\Delta S^\circ_{(g)}$  is always referred to as the same type of gas-phase reaction, so it can be considered to be same for various solvent molecules. Hence the difference in free energy of reaction in gas-phase for a solvent S and an arbitrarily selected solvent D equal to:

$$\begin{aligned} \Delta \Delta G^\circ_{(g)} &= \Delta G^\circ_{(g)} - \Delta G^\circ_{(g)} = \\ f (DN^S_{SbCl_5} - DN^D_{SbCl_5}) &= f \Delta DN_{SbCl_5} \end{aligned} \quad (9)$$

On the other hand according to equation (2) we obtain the following expression for differences in free energy of  $BiL_3$  in gas-phase for the given solvent  $\Delta G^\circ_{(g)}$  and the standard solvent D ( $\Delta G^D_{(g)}$ ):

$$\begin{aligned} \Delta \Delta G^\circ_{(g)} &= \Delta G^\circ - \Delta G^D + \Delta G_{solv}(L) - \\ &\Delta G^D_{solv}(L) + \Delta G^D_{solv}(BiCl_3 \cdot Sn) - \\ &\Delta G^D_{solv}(BiCl_3 \cdot DN) + \Delta G^\circ_{vap} - \Delta G^D_{vap} - \\ &\Delta G^\circ_{solv}(BiL_3) - \Delta G^D_{solv}(BiL_3) - \\ &\Delta G^\circ_{solv}(Cl) \end{aligned} \quad (10)$$

Combining equations (9) and (10) we get:

$$\begin{aligned} \Delta \Delta G^\circ_{(g)} &= f \Delta DN_{SbCl_5} = \Delta \Delta G^\circ_{solv}(L) + \\ &\Delta \Delta G^\circ_{solv}(BiCl_3 \cdot Sn) - \Delta \Delta G^\circ_{solv}(BiL_3) - \\ &\Delta \Delta G^\circ_{solv}(Cl) + \Delta \Delta G_{vap} \end{aligned} \quad (11)$$

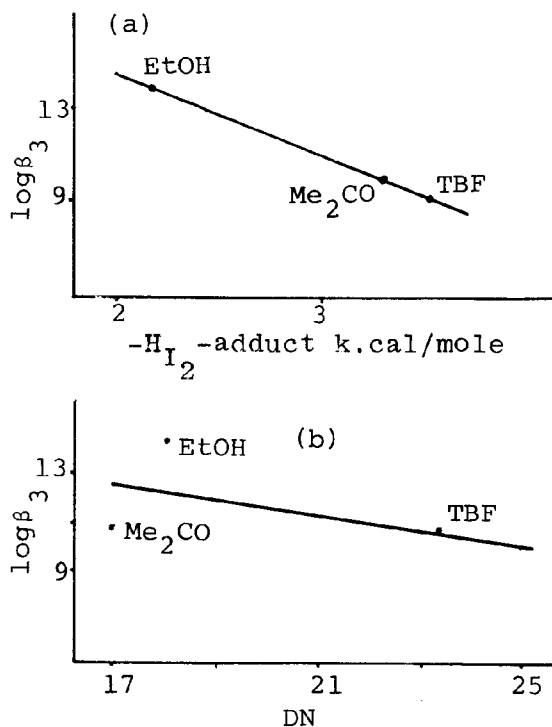


Fig. 2. Dependence of  $\log \beta_3$  on (a)  $-\Delta H_{I_2}$  adduct formation of the solvent with iodine and (b) DN of the solvent; for the complexation of Sb(III) with dsp.

Equation (11) can be preferred to equation (2) in certain respects because equation (11) contains relative values of free energy for various steps of the cycle (1), a number of which can be experimentally determined. moreover by considering the relative values of  $\Delta\Delta G^\circ$  we actually reduce the contributions due to entropy in complexation. From equation (11) the quantities  $\Delta\Delta G^\circ$ ,  $\Delta\Delta G^\circ_{vap}$  and  $\Delta\Delta G^\circ_{solv}(Cl^-)$  can directly be determined. The quantity  $\Delta\Delta G^\circ(Cl^-)$  has been thermodynamically determined<sup>□</sup> by using acetonitrile as the standard solvent. We use the same standard solvent while calculating  $\Delta\Delta G^\circ$  of various steps in the cycle (1). The values of  $\Delta\Delta G^\circ_{solv}(Cl^-)$  are summarised in table 2.

Standard free energy of vaporisation can be expressed by the following equation:

$$\Delta G^\circ_{vap} = -RT \ln p^s \quad (12)$$

and  $\Delta\Delta G^\circ_{vap}$  by the equation:

$$\Delta\Delta G^\circ_{vap} = -RT \ln p^s - RT \ln p^{CH_3CN} =$$

$$RT \ln \frac{p^{CH_3CN}}{p^s} \quad (13)$$

where  $p^{CH_3CN}$  and  $p^s$  are the vapor pressure at equilibrium of acetonitrile and the solvent respectively at  $T = 298^\circ K$ . The calculated values of  $\Delta\Delta G^\circ_{vap}$  are shown in table 3. The quantity  $\Delta\Delta G^\circ$  is calculated directly from the values of  $\beta_3$  through the common equation:

$$\Delta\Delta G^\circ = -RT \ln \beta_3 + RT \ln \beta_3^{CH_3CN} =$$

$$RT \ln \frac{\beta_3^{CH_3CN}}{\beta_3} \quad (14)$$

Lets consider the calculation of solvation energy of the ligand L. It has been demonstrated<sup>4</sup> that a very small proton of energy change due to ion transfer from gas-phase to solvent, can be attributed to specific ion-solvent interaction depending upon solvent nature. The basic contribution to solvation depending upon solvent nature. The basic contribution to solvation energy is due to dielectric polarization of the solvent and it depends only on the dielectric properties ( $\epsilon$ ) of the solvent:

$$[\Delta G^\circ_{solv}]_{dp} = -\frac{N(Ze)^2}{2r} \left( \frac{1-1}{\epsilon_s} \right) \quad (15)$$

The total value of  $\Delta G^\circ_{solv}(L^-)$  can conveniently be expressed as:

$$\Delta G^\circ_{solv}(L^-) = [\Delta G^\circ_{solv}(L^-)]_{dp} +$$

$$[\Delta G^\circ_{solv}(L^-)]_{sp} \quad (16)$$

Authors<sup>3,4</sup> are of the opinion that a change to relative values of  $\Delta\Delta G^\circ(L^-)$  the contribution to the energy of solvation of ions due to dielectric polarization may

Table 2.

Standard free energy of solvation of Cl<sup>-</sup> ion with respect to acetonitrile (T = 298° K)

Solvent	$\Delta G_{\text{solv}}^{\circ s} - \Delta G_{\text{solv}}^{\circ \text{CH}_3\text{CN}} = \Delta \Delta G_{\text{solv}}^{\circ} (\text{Cl}^-)$
MeCN	0
Me <sub>2</sub> CO	3.45
EtOH	-4.76
MeOH	-5.98
DMF	.22
DMSO	0

the data is taken from 3.

not be considered by taking it to be constant for a number of solvents having close dielectric permeabilities. However this factor becomes significant with solvents of low (ε) values reaching several Kcals/mole as is shown below. With the help of equation (15) we get:

$$[\Delta \Delta G_{\text{solv}}^{\circ}]_{\text{dp}} = \frac{N(Ze)^2}{2r} = \frac{\epsilon_{\text{CH}_3\text{CN}} - \epsilon}{\epsilon \epsilon_{\text{CH}_3\text{CN}}}$$

According to the basic theoretical considerations the specific solvation energy  $[\Delta G_{\text{solv}}^{\circ} (\text{L}^-)]_{\text{sp}}$  can be expressed as:

$$[\Delta G_{\text{solv}}^{\circ} (\text{L}^-)]_{\text{sp}} = \phi_L \phi_s \quad (18)$$

where  $\phi_L$ ,  $\phi_s$  functions depend upon the nature of the ion and the solvent  $[\Delta G_{\text{solv}}^{\circ} (\text{L}^-)]$  cannot be determined experimentally, however on the basis of equation (18) it can be demonstrated that this value will be proportional to the free energy of solvation of chloride ion. For Cl<sup>-</sup> ion it is equal to:

$$[\Delta G_{\text{solv}}^{\circ} (\text{Cl}^-)] = \phi_s \phi_{\text{Cl}^-} \quad (19)$$

From equations (18) and (19) we get:

Table 3.

Standard free energy of vaporisation of solvent S with respect to acetonitrile (T = 298 K)

Solvent	$\Delta G_{\text{vap}}^{\circ} (\text{g}) - \Delta G_{\text{vap}}^{\circ \text{CH}_3\text{CN}}$
MeCN	0
Me <sub>2</sub> CO	-0.54
EtOH	0.55
MeOH	0.04
DMF	1.88
DMSO	2.95

the data taken from reference 3.

$$\frac{[\Delta G_{\text{solv}}^{\circ} (\text{L}^-)]_{\text{sp}}}{[\Delta G_{\text{solv}}^{\circ} (\text{Cl}^-)]_{\text{sp}}} = \frac{\phi_L}{\phi_{\text{Cl}^-}} = \alpha_1 \quad (20)$$

and subsequently,

$$[\Delta G_{\text{solv}}^{\circ} (\text{L}^-)]_{\text{sp}} = \alpha_1 [\Delta G_{\text{solv}}^{\circ} (\text{Cl}^-)]_{\text{sp}} \quad (21)$$

Substituting equation (21) in (16) we get:

$$\Delta G_{\text{solv}}^{\circ} (\text{L}^-) = [\Delta G_{\text{solv}}^{\circ} (\text{L}^-)]_{\text{dp}} + \alpha_1 [\Delta G_{\text{solv}}^{\circ} (\text{Cl}^-)]_{\text{sp}} \quad (22)$$

After referring  $\Delta G_{\text{solv}}^{\circ} (\text{L}^-)$  to acetonitrile we have:

$$\Delta \Delta G_{\text{solv}}^{\circ} (\text{L}^-) = \frac{N(Ze)^2}{2r} \frac{\epsilon_{\text{CH}_3\text{CN}} - \epsilon_s}{\epsilon_s \epsilon_{\text{CH}_3\text{CN}}} + \alpha_1 [\Delta \Delta G_{\text{solv}}^{\circ} (\text{Cl}^-)] \quad (23)$$

The calculation of  $\Delta G_{\text{solv}}^{\circ} (\text{L}^-)$  demands detailed study. Equation (23) gives only the value of  $\Delta G_{\text{solv}}^{\circ}$  (ion solvation). Actually the molecule L<sup>-</sup> contains two hydrocor-



Table 4

Calculations of free energy of complexation in gaseous phase.

Solvent	$\log\beta_3$	$\Delta G^\circ$	$\Delta\Delta G^\circ$	$\Delta DN$	$\Delta\Delta G_{\text{solv}}^\circ(\text{Cl})$	$\Delta\Delta G_{\text{vap}}^\circ$	$\epsilon(25^\circ\text{C})$	$\frac{\epsilon_{\text{CH}_3\text{CN}} - \epsilon_s}{\epsilon_s \epsilon_{\text{CH}_3\text{CN}}}$
MeCN	13.11	-18	0	0	0	0	36.2	0
Me <sub>2</sub> CO	10.50	-14.5	3.5	2.9	3.45	-0.54	20.7	0.021
EtOH	14.40	-20	-2	3.8	-4.76	0.55	32.6	0.003
MeOH	14.30	-20	-2	4.8	-5.98	0.04	24.3	0.014
DMF	5.20	-7.6	10.4	11.9	1.22	1.88	36.1	0
DMSO	2.22	-3	15	15.7	0	2.95	46.1	-0.005

Putting (23), (26) and (29) in (11) we get the following equation for  $\Delta\Delta G_{(g)}^\circ$ :

$$\Delta\Delta G_{(g)}^\circ = f \Delta DN = \Delta\Delta G^\circ + \frac{N(Ze)^2}{2r}$$

$$\frac{\epsilon_{\text{CH}_3\text{CN}} - \epsilon_s}{\epsilon_s \epsilon_{\text{CH}_3\text{CN}}} + \alpha [\Delta\Delta G_{\text{solv}}^\circ(\text{Cl})] +$$

$$+ f' \Delta DN - \beta_1 \Delta\Delta G_{\text{vap}}^\circ - f'' \Delta DN -$$

$$\Delta\Delta G_{\text{solv}}^\circ(\text{Cl}) + \Delta\Delta G_{\text{vap}}^\circ \quad (30)$$

Or

$$\Delta\Delta G^\circ = f' \Delta DN - \frac{N(Ze)^2}{2r} \frac{\epsilon_{\text{CH}_3\text{CN}} - \epsilon_s}{\epsilon_s \epsilon_{\text{CH}_3\text{CN}}} -$$

$$(\alpha-1) \Delta\Delta G_{\text{solv}}^\circ(\text{Cl}) - (1-\beta) \Delta\Delta G_{\text{vap}}^\circ \quad (31)$$

The above equation can conveniently be expressed as:

$$\Delta\Delta G^\circ = f \Delta DN - \frac{N(Ze)^2}{2r} \frac{\epsilon_{\text{CH}_3\text{CN}} - \epsilon_s}{\epsilon_s \epsilon_{\text{CH}_3\text{CN}}} -$$

$$a \Delta\Delta G_{\text{solv}}^\circ(\text{Cl}) - b \Delta\Delta G_{\text{vap}}^\circ \quad (32)$$

where

$$a = \alpha-1, b = 1-\beta_1 \text{ and } f - f' - f'' = f$$

Equation (32) can be used as a correlation equation in which it is essential to find out the optimum values of three parameters  $f$ ,  $a$  and  $b$ , from experimental data. From these values it will be possible to calculate, the values of free energy of complex formation in gaseous phase, although semi-empirically. These values are theoretically more reliable than the directly calculated  $\Delta G^\circ$  in the given solvent. The calculated values of these parameters are summarised in table 4. with the help of these values (eq. 32), system of following equations can be written as:

$$4.55 = 2.9f - 3.45a + 0.54b$$

$$- 1.85 = 3.8f + 4.76a - 0.55b$$

$$- 1.30 = 4.8f + 5.98a - 0.04b \quad (33)$$

$$10.40 = 11.9f + 1.22a - 1.88b$$

$$14.75 = 15.7f - 2.95b$$

With the help of a computer the best values of  $f$ ,  $a$  and  $b$  giving minimum standard deviation, were calculated to be equal to  $f = 0.9$ ,  $a = -0.9$  and  $b = 0.1$ . In this way an expression for free energy of complex formation in gaseous phase can be presented according to the equation (30) and (32) by using the values of parameters  $f$ ,  $a$  and  $b$ , as:

$$\Delta\Delta G_{(g)}^\circ = \Delta\Delta G^\circ + \frac{N(Ze)^2}{2r} \frac{\epsilon_{\text{CH}_3\text{CN}} - \epsilon_s}{\epsilon_s \epsilon_{\text{CH}_3\text{CN}}} -$$

$$0.9 \Delta\Delta G_{\text{solv}}^\circ(\text{Cl}) + 0.1 \Delta\Delta G_{\text{vap}}^\circ$$

$$0.9 \Delta\Delta G_{\text{solv}}^\circ(\text{Cl}) + 0.1 \Delta\Delta G_{\text{vap}}^\circ = 0.9 \Delta DN \quad (34)$$

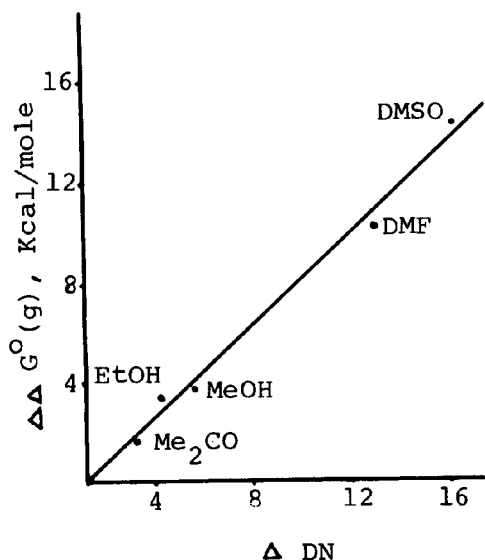


Fig. 3. Dependence of  $\Delta\Delta G_{(g)}^{\circ}$  upon  $\Delta DN$ .

The values of free energy of complex formation in gaseous phase obtained from equation are summarised in table 5.

A plot of dependence of free energy of complexation in gaseous phase on DN (eq.34) is presented in figure (3). While comparing the dependence in figure (1) to that of figure (3) (where the value of log are proportional to free energy of complex formation in solution is the function of DN) we note that if we use gas phase, a significant improvement in the correlation is observed.

The above discussions lead to the conclusion that empirical scales of solvent donicity generally provide for quantitative determination of equilibrium constant dependability on the nature of the solvent. However the correlation with different scales is equally satisfying and the selection of an optimum scale (scale priori) is not possible due to the existence of a number of unknown contributions to the total free energy observed for complexation. An account for these contributions and a shift to gas-phase values is possible on the basis of semiempirical approach (discussed here) giving more accurate determination of relative dependability of stability constant on the donor properties of the solvent.

Let us consider in detail the practical aspects using the above approach. The quantities (values)  $f$ ,  $a$  and  $b$  cannot be theoretically determined. Thus using equation

Table 5

Free energy of complex formation in gaseous phase.

Solvent	$\Delta\Delta G_{(g)}^{\circ}$ , KCal/mole
Me <sub>2</sub> CO	1.45
MeOH	3.55
EtOH	3.10
DMF	9.50
DMSO	15.05

(32) we actually go from a simple one-parameter correlation ( $\Delta G_{\text{compl}}^{\circ}$  or log K with DN) to a more complicated three-parameter equation. This in fact complicates the mathematics of results. Moreover the values  $\Delta\Delta G_{\text{soln}}^{\circ}$  (Cl) is known for relatively small number of solvents. In case of complicated organic molecules the indeterminability still increases when the ionic radius of the ligand is assessed. All these factors make the application of equation (32) difficult for important practical cases of complexation used extensively in analytical chemistry of complicated organic reagents. In this regard a significant interest lies in developing a simpler but effective approach to the quantitative determination of solvent effect on the stability constants.

We are of the opinion that it is helpful in the present situation to study the possibility of bettering the correlation  $\Delta G_{\text{compl}}^{\circ}$  with DN by fully introducing the linearly proportional member of Acceptor number (AN — characterised by the solvating ability of the solvent with respect to nucleophilic or anionic species; such species being either molecules or ligand anions which like metal ions desolvate during complexation). Earlier in this report during the discussions of quantitative effect of solvent on the stability constants we have proposed that the desolvation energy of the ligand can be neglected compared to the energy of other processes constituting the overall process of complexation. While allowing this we had drawn the conclusion regarding the possibility of a linear correlation of log  $\beta_3$  with DN which in fact reflects the actual dependence of solvation of cationic centre from DN. By analogy to that it can be said that the solvation of the ligand on the basis of LCE



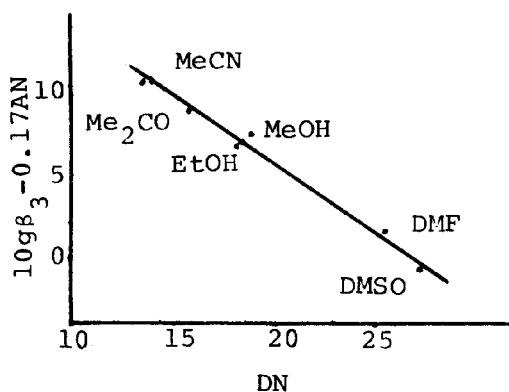


Fig. 4. Dependence of  $\log \beta_3 - 0.17 AN$  upon DN

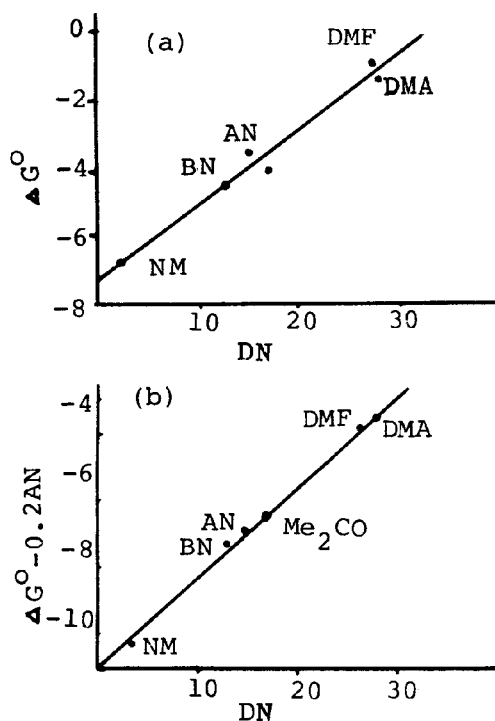


Fig. 5. (a) Dependence of  $\Delta G^0$  upon DN (b) Dependence  $\Delta G^0 - 0.2 AN$  upon DN.

should correlate with AN. In this way the desolvation of ligand can be expressed in the form of a correlation of  $\log \beta_3$  with the solvent properties as:

$$\log \beta_3 = \alpha DN + \beta AN + \gamma \quad (35)$$

The resulting equation (35) is strikingly similar to (32) where the factor responsible for ligand desolvation has the form a  $\Delta \Delta G^0_{\text{solv}}(\text{Cl}^-)$  and as described the quantity  $\Delta \Delta G^0_{\text{solv}}(\text{Cl}^-)$  correlate with AN.

The use of data, in table 1, regarding solvent effect upon  $\log \beta_3$  for diphenyldiselenophosphate complexes of bismuth (III) with the help of equation (31) we get an expression in the form of a correlation:

$$\log \beta_3 = 20 - 0.7 DN + 0.17 AN \quad (36)$$

Figure five shows the dependence of  $\log \beta_3 - 0.17 AN$  on DN with a slope  $\alpha = 0.7$  according to the equation (36). A comparison of figure (5) with figure (1) shows that the introduction of AN significantly improve the correlation of  $\log \beta_3$  ( $S = 0.5$  and  $2.1$  respectively for both the figures).

For a general verification of equation (35) we have considered the data available in literature regarding the effect of solvent on the complexation constant expressed below<sup>4</sup>:

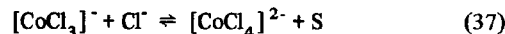


Figure 6, depicts the dependence of  $\Delta G^0$  of the reaction (37) upon DN, having almost linear correlation and is written as:

$$\Delta G^0 = 0.2 DN - 7.1; S = 0.49$$

While that two-parameter equation worked out in this report gives:

$$\Delta G^0 = 0.25 DN + 0.2 AN - 113.; S = 0.27$$

Graphically the dependence  $\Delta G^0 = 0.2 AN$  on DN (figure 5) also improves the correlation by considerably reducing the value of S, than simple correlation with DN.

#### Acknowledgement

The authors are extremely grateful to Dr. A.K. Iatsimirskii, Senior Research Officer, Faculty of Chemistry, Moscow State University; for processing the data on the computer.

## References

1. William B. Jensen, *Chem. Reviews*, **78**, 1 (1978).
2. Rafee Arain, *Sind Univ. Res. Jour. (Sci. Ser.)*, **X**, 103 (1977).
3. U. Mayer, *Pure and Appld. Chem.*; **41**, 291, (1975).
4. U. Mayer and V. Gutmann and W. Gerger; *Monatsch. Chem.*, **106**, 1235 (1975).