Bull.Chem.Soc.Ethiop. **1992**,6(2) 123-126.

FURTHER OBSERVATIONS REGARDING LINEAR RELATIONSHIPS IN GIBBS ENERGIES OF SOLVATION

Theodros Solomon
Department of Chemistry, Addis Ababa University, P.O.Box 1176, Addis Ababa, Ethiopia.

(Received August 5, 1992; revised December 30, 1992)

ABSTRACT: It is shown that, for a pair of related ions, (e.g. the alkali metal ions K^+ and Rb^+) the corresponding Gibbs energies of solvation in a series of solvents are linearly related to each other with a slope of unity, whereas, for a pair of unrelated ions, (e.g. a cation K^+ and an anion Cl^-), the linear relationships in the corresponding Gibbs energies of solvation fall on two separate lines - one for values in dipolar aprotic solvents, and another in hydrogen-bonded solvents.

INTRODUCTION

In connection with studies on Gibbs energies of transfer of ions across the interface between two immiscible electrolyte solutions (ITIES), linear Gibbs energy relationships (LGER) were recently proposed [1-2]. It was shown that:

(a) within the (appreciable) limits of error of the literature data, there is a linear relationship between the Gibbs energy of solvation of a series of related ions in one solvent (α) and the corresponding values for the same series in another solvent (β), this linear relationship having a slope of unity, i.e.

$$\Delta G^{\alpha}_{solv,i,j,..} = \Delta G^{\beta}_{solv,i,j,..} + \text{const} \qquad (1)$$

(b) there is a linear relationship between ln D (diffusion coefficient of an ion) and its Gibbs energy of solvation, and

(c) there is a linear relationship between ln $k^{\alpha\rightarrow\beta}$ (the rate constant for the transfer of ions from phase α to phase β) and the corresponding Gibbs energies of transfer.

A consequence of observation (a) above is that a similar linear relationship should be - and, indeed, is - observed between the Gibbs energies of solvation of an ion *i* in a series of solvents, and the corresponding values for another related ion *j* in the same series of solvents; in other words,

$$\Delta G^{\alpha,\beta,..}_{solv,i} = \Delta G^{\alpha,\beta,..}_{solv,j} + \text{const.} \qquad (2)$$

DISCUSSION

The proof that Eq. (2) follows from Eq. (1) can be seen by reference to an elementary property of matrices. In order to discuss in matrix terms, a slightly different notation will be used below.

Consider a 4 x 4 matrix where, in each column, are placed the values of the Gibbs energies of solvation of four ions in a given solvent, and in each row are placed the Gibbs energies of solvation of a given ion in four solvents. Using m_{ij} for $\Delta G^{j}_{solv,i}$ this matrix can be represented as:

$$M = \begin{bmatrix} m_{11} & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{bmatrix} \qquad (3)$$

If it is observed that any two columns are linearly related to each other, with a slope equal to unity, then, expressing all columns in terms of the first, one may generally write for M:

$$M = \begin{bmatrix} m_{11} + a_1 & m_{11} + a_2 & m_{11} + a_3 & m_{11} + a_4 \\ m_{21} + a_1 & m_{21} + a_2 & m_{21} + a_3 & m_{21} + a_4 \\ m_{31} + a_1 & m_{31} + a_2 & m_{31} + a_3 & m_{31} + a_4 \\ m_{41} + a_1 & m_{41} + a_2 & m_{41} + a_3 & m_{41} + a_4 \end{bmatrix} \qquad (4)$$

where the a's are constants, which may also assume a value of 0. The equation of a straight line relating any two columns in M can therefore be written as:

$$Y = X + (a_l - a_k) \qquad (5)$$

where X and Y represent corresponding elements in any two columns of the matrix M, and $(a_l - a_k)$ is the constant difference between the two columns. This is an alternative expression for Eq. (1). An observation of the matrix above clearly shows that a similar linear relationship also holds for the rows of the matrix, namely:

$$Y = X + (m_{l1} - m_{k1}) \qquad (6)$$

where X and Y are corresponding elements in any two rows of M and $(m_{l1} - m_{k1})$ is now the constant difference between the two rows of M. Eq. (6) is an alternative expression for Eq. (2).

Similarly, it can be shown that the converse is also true, namely that Eq. (1) follows from Eq. (2), as long as the linear relationship has a slope of unity.

Returning to Gibbs energies of solvation, Fig. (1) is an example of a plot of Eq. (2) for a pair of alkali metal ions (K^+ and Rb^+) in a variety of solvents. This plot may also be drawn in terms of the Gibbs energies of transfer $\Delta G_{t,i}^{w \to o}$ from water (w) to an organic solvent (o) since $\Delta G_{t,i}^{w\rightarrow o} = \Delta G_{solv,i}^{o} - \Delta G_{solv,i}^{w}$. The axes in the plot above would then be simply shifted by a constant amount, equal to $\Delta G_{solv,i}^{w}$. The conclusion thus remains unaffected. Note that the solvents in the above plot may be classified (following Marcus [4]) as dipolar aprotic or hydrogen-bonded, and that the linear relationship holds irrespective of the nature of the solvent. However, this is not necessarily the case if the ΔG_{solv} values of two unrelated ions (e.g. a cation K^+ and an anion Cl^-) are plotted against each other. Literature data [5] show that two separate lines are found, one for values in dipolar aprotic solvents, and another in hydrogen - bonded solvents. An example of such a plot is shown in Fig. 2. That two separate lines are found in such a situation is not too surprising since one is comparing, first of all, the solvation of a cation with that of an anion, and secondly, the solvation of ions (particularly anions) has been shown [6-10] to be dependent on the nature of the solvent, i.e. whether the solvent is H-bonded (protic) or is dipolar aprotic. This result calls to mind another plot reported in the literature [11] of the solubility of electrolytes *versus* ε^{-1} (dielectric constant) in which two separate lines of differing slopes were obtained, one for alcohols (H-bonded) and another for ketones (dipolar aprotic).

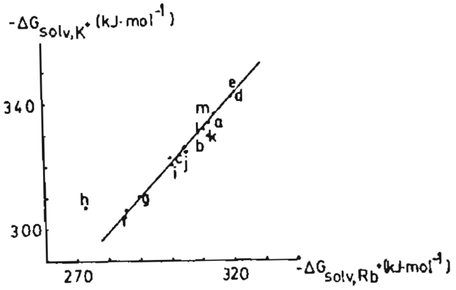

Fig. 1 Gibbs energy of solvation of K^+ *versus* Gibbs energy of solvation of Rb^+ in a variety of solvents. (Hydrogen - bonded solvents: a: methanol, b: ethanol, c: propanol, d: formamide, e: N-methylformamide; dipolar aprotic solvents f: 1,1-dichloroethane g: 1,2-dichloroethane, h: tetrahydrofuran, i: acetone, j: acetonitrile, k: nitromethane, l: dimethylformamide, m: dimethylsulfoxide.) (Data from Ref. (5))

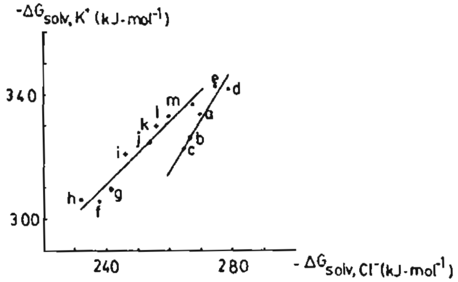

Fig. 2. Gibbs energy of solvation of K^+ *versus* Gibbs energy of solvation of Cl^- in a variety of solvents. (Letters as in Fig. 1.) (Data from Ref. (5))

In general, in all protic solvents, cations are solvated by interactions with the negative end of the solvent dipoles, whereas anions are solvated by interactions with the positive end of the solvent dipoles. In protic solvents, anions are solvated via H-bonding, and by dispersion interactions in dipolar aprotic solvents. Also, in dipolar aprotic solvents, anions are less solvated than cations. These generalizations can help explain the single linear plot for K^+ *versus* Rb^+ (Fig. 1), and the two different linear plots for K^+ *versus* Cl^- (Fig. 2).

Such linear relationships are important in predicting Gibbs energies of solvation of ions, since the results are tantamount to stating that :

(a) For a series of related ions, (e.g. alkali metal ions) there is always a constant difference between their ΔG_{solv} values in one solvent and the corresponding values in another solvent; and

(b) There is always a constant difference in the ΔG_{solv} values for a pair of related ions in a series of solvents.

(c) For unrelated ions (e.g. a cation K^+ and an anion Cl^-), linear plots in the corresponding ΔG_{solv} are found only in a series of related solvents (e.g. H-bonded or dipolar aprotic). The two series of solvents give rise to two respective linear plots for the same pair of unrelated ions.

Further work is in progress to test these generalizations for a variety of systems and relate them to ion and solvent properties.

ACKNOWLEDGEMENTS

Fruitful discussions with Dr B. Hundhammer of the Department of Chemistry and with Ato Tewodros Amdeberhan of the Department of Mathematics (AAU) are gratefully acknowledged.

REFERENCES

1. Solomon, T. *J. Electroanal. Chem.* **1991**, 313, 29.
2. Solomon,T. *Bull. Chem. Soc. Ethiop.* **1991**, 5, 93.
3. Abraham, M.H.; Liszi, J. *J. Chem. Soc., Farad. Trans. I*, **1978**,74, 1604.
4. Marcus, Y. *An Introduction to Liquid State Chemistry*, Wiley, London: 1977.
5. Marcus, Y. *Pure and Appl. Chem.*, **1983**, 55, 977.
6. Burgess, J. *Metal Ions in Solution*, Ellis Horwood, Chichester: 1978.
7. Burger, K. *Solvation, Ionic and Complex Formation Reactions in Non-aqueous Solvents*, Elsevier, Amsterdam: 1983.
8. Popovych, O.; Tomkins, R.P.T. *Nonaqueous Solution Chemistry*, Wiley, New York: 1981.
9. Parker, A.J. *Quart. Rev.* **1962**, 16, 163.
10. Parker, A.J. *Chem. Rev.* **1969**, 69, 1.
11. Izmaylov, N.A.; Chernyi, V.S. *Zhur. Fiz. Khim.* **1959**, 33, 127; quoted in Ref.[6], p.27.