A MOLECULAR THEORY OF SETCHENOV'S SALTING-OUT PRINCIPLE AND APPLICATIONS IN MIXED-SOLVENT ELECTROLYTE SOLUTIONS

Lloyd L. Lee

School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, OK 73019, U.S.A.

[ABSTRACT]

An exact molecular theory is developed to express the salting-out behavior of solute species in mixed-solvent (more than one solvent) electrolyte solutions. The starting point is the Kirkwood-Buff solution theory. The Setchenov constant can be shown to be a special case (at infinite dilution) of the general theory. The new formula involves the partial molar volumes of the components and the isothermal compressibility of the medium. In addition, it contains the direct correlation function integrals (DCFI) for solvent-salt interactions. Furter's theory of relative volatilities is shown to be related to Setchenov's equation and the molecular-based equation. All these equations express the affinities of the solvent and cosolvents toward the salt in the solution. Low affinity (for a particular solvent-salt pair) means salting-out of this solvent. When combined with the Gibbs-Duhem relation, the affinity equations result in a differential equation for the activity of a single solvent which can be numerically solved. This affords a means of obtaining the activities of solvents individually in the mixture. We test the new approach for two ternary solutions: *methanol-water-LiBr* and *methanol-water-LiCl*, by applying an empirical affinity equation. For the ionic activities, we use the mean-spherical approximation (MSA) expressions. Comparison with experimental data shows that the agreement is close for the vapor-liquid equilibria of these ternary systems. Generalization to higher-component systems is outlined.

I. Introduction

The effects of salt addition on the solubility of gases and other solutes in aqueous and nonaqueous solutions are of considerable industrial and theoretical importance. In separation processes such as extractive distillation, azeotrope distillation (Furter and Cook 1967, Furter 1972), extractive crystallization (Weingaertner 1991), biofluid processing (e.g., two-phase protein partitioning (Walters 1985)), or in geological formations (Harvey and Prausnitz 1989) (e.g., petroleum reservoir), salt effects are necessary and required information. In 1889, Setchenov published a simple rule that at small gas solubilities, the dissolved gas, *g*, in a saline solution, x_g' (mole fraction of gas), is related to its solubility at same temperature T_0 in the clean (salt-free) solution, x_g^0 (note that we have changed the units of concentration from *molality* to *mole fraction* here, for ease of comparison subsequently) by

$$\ln\left(\frac{x_g^0}{x'_g}\right) = k_S\, x_s \tag{1.1}$$

where x_s is the mole fraction of the salt, *s*. k_S is called the Setchenov constant. It says that the "decrease" in logarithm of the gas solubility x_g' is linearly related to the content of salt in the solution. Depending on the sign of k_S, the solubility of the gas can be either decreased (*salting-out*), for positive k_S; or increased *(salting-in*), for negative k_S. This rule seems to work well for a number of salt solutions and for gases such as He, H_2, N_2, O_2, argon, CH_4, and C_2H_6 (Pawlikowski and Prausnitz 1983). Later, it has been realized that this k_S is not a constant of x_s. Eq.(1.1) is nonlinear in x_s beyond 5 M or at mole fraction $x_s > 0.1$.

In a separate development, Furter and coworkers (Johnson and Furter 1960) have used

the relative volatilities in developing the salt effects in mixed-solvent electrolyte solutions (more than one solvent, e.g., water plus methanol with salt). For example, for the saline solution methanol (a) +water (b) + LiBr (s), the relative volatility, α_s, is defined as (here a over b)

$$\alpha_s \equiv \frac{(y_a/y_b)}{(x_a/x_b)} \tag{1.2}$$

Namely, for a vapor-liquid system in coexistence, α_s is the ratio of the mole fractions y_a/y_b of the solvents in the vapor phase over x_a/x_b in the liquid phase. Thus when α_s is greater than 1, a is the more volatile solvent, vice versa. In the absence of salt x_s=0, we have only methanol+water for this example. This salt-free solution is called a *clean solution*. The relative volatility α_0 will be $\alpha_0 \equiv (y_a^0/y_b^0)/(x_a^0/x_b^0)$ The superscript 0 denotes clean solution properties. Johnson and Furter (1960) say

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = k_F\, x_s \tag{1.3}$$

The constant k_F is called the Furter constant. The statement prescribes that "the logarithm of the saline α_s over the clean α_0 vary linearly with salt content in the solution". This has again been shown to be successful for many mixed-solvent salt solutions (Furter and Cook 1967, Furter 1972). However, experimental data show that eq.(1.4) tends to fail for concentrated salt solutions. There is nonlinearity in the relative volatility ratio with respect to x_s at high salt contents. For some solutions, deviations already start at salt mole fraction $x_s > 0.1$. These observations prompt us to ask what is the *correct relation between all these solution quantities*? Why does linearity fail? What is the theoretical basis of the solubility of any solute in a mixed-solvent electrolyte environment?

In the present work, we shall combine principles from four separate disciplines and integrate them for use in mixed-solvent electrolyte systems: (i) the *thermodynamic* equation of Gibbs-Duhem for multicomponent mixtures; (ii) the affinity principle between solutes and solvents, i.e., preferential solvation and association in multi-solvent salt solutions as manifested in the relative solubility change (a *physicochemical* principle on properties, Setchenov's equation being one example of this principle); (iii) the Kirkwood-Buff 1951 solution theory (a theory connecting micro- and macro-properties, from *molecular correlation functions* to fluctuation-compressibility derivatives); and (iv) the *integral equation*: Mean Spherical Approximation (MSA, Blum and Høye 1977) for primitive model electrolytes (and the results for the ionic activity coefficients). First, we attempt to show that there is a molecular thermodynamic basis for this affinity behavior that is general and can be shown from its derivation to be "exact". This is based on the Kirkwood-Buff theory. The Setchenov and Furter affinities can be interpreted in terms of the molecular-based formulas and are special cases of the latter upon making simplifying assumptions. The aim is to answer the question: "what is the correct solubility behavior due to ions in solvents that is not subject to linearity constraints?" Second, the other two principles (i & iv) are used in constructing a differential equation algorithm for calculating multi-solvent electrolyte vapor-liquid equilibria (VLE).

The paper is divided into two parts: a molecular theoretical part (Section III), and an application part (Section IV). The two can be taken independently: the theory establishes the exact solvent affinity relation as derived from the Kirkwood-Buff theory. It involves the direct correlation function integrals (DCFI's). The DCFIs could be obtained from solving an integral equation (e.g., the hypernetted chain equation, HNC, Morita 1958) or

empirically from solution property data. In applications, we demonstrate by calculating the activities in mixed-solvent electrolytes via a combined Gibbs-Duhem/affinity algorithm, as an alternative to the conventional excess free energy route (the latter first postulates a free energy model for the entire solution, then derives the activity coefficients by thermodynamic differentiation). Some recent works (Raatschen, Harvey, and Prausnitz 1987, Macedo et. al 1990, Zerres and Prausnitz 1994, Kolker and de Pablo 1995a) belong to the free energy of solution approach. Kolker and de Pablo 1995b and 1996 also formulated an integation scheme from the Gibbs-Duhem equation, similar in spirits to the approach of Wu and Lee 1992 and to the present formulation. Our resulting equation (3.9) will be called the *algorithm*. We shall use data to construct *empirical* expressions of the affinity relation for use in the algorithm (not from the DCFIs). We then apply the algorithm to the determination of the VLE of two mixed-solvent systems: *water-methanol-LiBr* and *water-methanol-LiCl.* The present results are more general than Wu and Lee 1992). We extend to the lithium bromide solution, an absorbent widely used in commercial absorption chillers (Lane and Huey 1995).

In Section II, we examine the relation between the Setchenov equation (1.1) and the Furter equation (1.4). In Section III we deive the molecular formulas for solvent affinity. In addition, we show how one can use Gibbs-Duhem relation to contruct a procedure for calculating the activity coefficients. In Section IV, we apply to two alcohol-water-salt systems. Section V draws the conclusion.

II. Relation between Setchenov and Furter Equations

We shall show here that the Setchenov equation (1.1) is a simplified case of the Furter eq.

(1.4). Consider an isopiestic experimental setup (Platford 1979) where two vessels ("0" and "1") are connected through a common vapor space. In vessel "0", we have a clean solution $a+b$ with no salt. In vessel "1", we have a saline solution $a+b+s$. The whole system is maintained at temperature T_0. The system is allowed to reach equilibrium at a pressure P_0.

Since the chemical potential of the species a is common to the vapor and two liquid phases

$$\mu_a^0 = \mu_a^v = \mu_a^{'} \tag{2.1}$$

where superscript 0 denotes clean solution (liquid phase) properties, superscript ' denotes saline solution (liquid phase) properties, and superscript v denotes the vapor phase properties. Pawlikowski et al. (1983) have shown that in the limit of small solubilities of a (and low x_s), the Setchenov principle namely eq.(1.1) holds.

In terms of relative volatilities, since $y_a^{'} = y_a^0$ and $y_b^{'} = y_b^0$ (both liquids are in equilibrium with a common vapor phase), we have

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = \ln\left(\frac{(y_a^{'}/y_b^{'})/(x_a^{'}/x_b^{'})}{(y_a^0/y_b^0)/(x_a^0/x_b^0)}\right) = \ln\left(\frac{(x_a^0/x_b^0)}{(x_a^{'}/x_b^{'})}\right) = \; k_F\, x_s \tag{2.2}$$

In the limit $x_a^{'} \to 0$, and $x_b^{'} \approx 1 \approx x_b^0$ (i.e., at infinite dilution), eq.(2.2) reduces to

$$\ln\left(\frac{x_a^0}{x_a^{'}}\right) = \; k_F\, x_s, \qquad (x_s \to 0,\;\; x_a^{'} \to 0) \tag{2.3}$$

This is precisely the Setchenov equation (1.1). Setchenov's equation is the limit of the Furter equation (1.4) when all "solute" species a and s approach infinite dilution in a

solvent b. Thus $k_F = k_S$. However, away from infinite dilution, the two equations indicate different principles.

Eq.(2.2) says if $k_F > 0$, y_a is enriched, and the solvent a "escapes" to the vapor phase. This behavior is called *salting-out* of species a. On the other hand, if $k_F < 0$, species a will prefer to stay in the liquid (its affinity with the salt is stronger), while b is salted out. Thus Furter's k_F is an *affinity principle*, namely it reflects the strengths of affinity of the solvents a and b towards the salt s. Higher affinity of a towards s over affinity of b towards s will induce a to stay in the liquid solution (*salted-in*), while expelling b (*salted-out*). The affinity principle is independent of the usual thermodynamic relations (e.g., Gibbs-Duhem relation). It is a physico-chemical principle related to the "properties" or "molecular interactions" between molecules of different species (or ions) that are crucial in determining the selectivity in mixed-solvent phase equilibria.

We have shown in a previous paper (Wu and Lee 1992), that the Furter equation is actually a first order Taylor's expansion of the difference of the activity coefficients for species a and b:

$$\frac{\partial \ln\gamma_a}{\partial x_s} - \frac{\partial \ln\gamma_b}{\partial x_s} \approx k_F, \qquad (\textit{to first order}) \tag{2.4}$$

This recognition will assist in the formulation of a molecular theory of solvent affinity.

II. A Molecular Theory of Solvent Affinity

In the Kirkwood-Buff (1951) theory of solutions, the derivatives of the chemical potentials or the activity coefficients can be expressed in terms of the Kirkwood-Buff

fluctuation integrals G_{ab} or the direct correlation function integrals (DCFI) C_{ab}. These factors are microscopic (molecular) in nature (Lee, Debenedetti, and Cochran 1991)

$$C_{ab} \equiv \rho \int d\mathbf{r}\, c_{ab}(r) \tag{3.1}$$

where $c_{ab}(r)$ is the direct correlation function for the pair of molecules of species a and b, and ρ is the number density of the total solution. It has been shown by O'Connell (1990) that the derivatives of the activity coefficient $\ln\gamma_a$, depending on the choice of fixed state parameters, assume the forms

$$n\left.\frac{\partial \ln\gamma_a}{\partial n_s}\right]_{T,V,N_{k\neq s}} = (1 - C_{as})\,, \quad or \qquad n\left.\frac{\partial \ln\gamma_a}{\partial n_s}\right]_{T,P,N_{k\neq s}} = (1 - C_{as}) - \frac{\rho \bar{V}_a \bar{V}_s}{kTK_T} \tag{3.2}$$

Similarly,

$$n\left.\frac{\partial \ln\gamma_b}{\partial n_s}\right]_{T,V,N_{k\neq s}} = (1 - C_{bs})\,, \quad or \qquad n\left.\frac{\partial \ln\gamma_b}{\partial n_s}\right]_{T,P,N_{k\neq s}} = (1 - C_{bs}) - \frac{\rho \bar{V}_b \bar{V}_s}{kTK_T}$$

where $n = n_a + n_b + n_s$ is the total number of molecules; $\bar{V}_i$ is the partial molar volume (PMV) for $i = a,b,s$; and $K_T = -(1/V)\partial V/\partial P\,|_T$ is the isothermal compressibility. We see that differentiation at constant volume gives a different expression than differentiation at constant pressure (a well-known distinction). When we take the differences

$$n\left.\frac{\partial \ln\gamma_a}{\partial n_s}\right]_{T,V,N_{k\neq s}} - n\left.\frac{\partial \ln\gamma_b}{\partial n_s}\right]_{T,V,N_{k\neq s}} = -C_{as} + C_{bs} \tag{3.3a}$$

and

$$n\left.\frac{\partial \ln\gamma_a}{\partial n_s}\right]_{T,P,N_{k\neq s}} - n\left.\frac{\partial \ln\gamma_b}{\partial n_s}\right]_{T,P,N_{k\neq s}} = -C_{as} + C_{bs} - \frac{\rho \bar{V}_s(\bar{V}_a - \bar{V}_b)}{kTK_T} \tag{3.3b}$$

Thus we obtain expressions for the differences of the derivatives of the activity coefficients of two solvents in terms of the molecular (microscopic) C_{ij} and thermodynamic (partial molar volumes and isothermal compressibility) quantities. We note that the two equations in (3.3), one isochoric, the other isobaric, are exact expressions, based on the Kirkwood-Buff solution theory. No approximations have been made. We can easily show that the Furter k_F is expressed as

$$k_F\,(1-x_s)+x_s n\frac{\partial k_F}{\partial n_s} = -C_{as}+C_{bs}-\frac{\rho\bar{V}_s(\bar{V}_a-\bar{V}_b)}{kTK_T}, \tag{3.4a}$$

In the limit $x_s \to 0$, at low salt concentration

$$k_F = \lim_{x_s\to 0}\left[C_{bs}-C_{\alpha_s}\right]+\frac{\rho\bar{V}_s(\bar{V}_b-\bar{V}_a)}{kTK_T}, \tag{3.4b}$$

This identification is meaningful, in that k_F, the center piece of Furter's principle, is now accessible through molecular and thermodynamic quantities. Immediately we observe that k_F is not a *constant*, because the DCFI's and the PMV's are variables of composition. The partial molar volumes $\bar{V}_a-\bar{V}_b$ will determine the sign of k_F: positive means salting-in, and negative means salting-out of the solvent a. This is in conformity with the observations of Long and McDevit (1952). The difference in activity derivatives is an indication of preferential solvation.

We have expressed the Furter k_F in terms of molecular variables. Although eqs.(3.3) are exact, the problem is how to obtain the quantities therein. One way is to use integral equation theories (e.g., HNC) for the DCFI's, and use experimental data for the PMV's and K_T. We do not intend to do this here. For demonstration of the algorithm, we shall

use fitted formulas.

Now we change course: we shall use the principles *Gibbs-Duhem* and *MSA* cited in the Introduction to devise a procedure for calculating the solvent activities γ_a, assuming that we already have knowledge of the affinities.

Algorithm for Calculating Activity Coefficients

We shall combine (3.3b) with the Gibbs-Duhem (GD) relation. For example, in a three-component $a+b+s$ system, GD gives

$$n_a \frac{\partial \ln\gamma_a}{\partial n_s} + n_b \frac{\partial \ln\gamma_b}{\partial n_s} + n_s \frac{\partial \ln\gamma_s}{\partial n_s} = \beta V^E \frac{\partial P}{\partial n_s} \tag{3.5}$$

where V^E is the excess volume, $\beta = 1/kT$, and k = Boltzmann constant. Multiplying (3.3b) by x_b,

$$n_b \frac{\partial \ln\gamma_a}{\partial n_s} - n_b \frac{\partial \ln\gamma_b}{\partial n_s} = x_b \left(C_{bs} - C_{as} + \frac{\rho \bar{V}_s (\bar{V}_b - \bar{V}_a)}{kTK_T} \right) \tag{3.6}$$

and adding to (3.5), we can eliminate the cosolvent term n_b in the GD expression (noting that $dP = 0$ for this process):

$$(n_a + n_b) \frac{\partial \ln\gamma_a}{\partial n_s} + n_s \frac{\partial \ln\gamma_s}{\partial n_s} = x_b \left(C_{bs} - C_{as} + \frac{\rho \bar{V}_s (\bar{V}_b - \bar{V}_a)}{kTK_T} \right) \tag{3.7}$$

or

$$\frac{\partial \ln\gamma_a}{\partial n_s} = -\frac{n_s}{n_a + n_b} \frac{\partial \ln\gamma_s}{\partial n_s} + \frac{x_b}{n_a + n_b} \left(C_{bs} - C_{as} + \frac{\rho \bar{V}_s (\bar{V}_b - \bar{V}_a)}{kTK_T} \right) \qquad (T,\ P\ constant) \tag{3.8a}$$

The dP term disappears due to constant pressure in (3.3.b). However, if (3.3a) is used (i.e., at constant volume), we have instead

$$\frac{\partial \ln\gamma_a}{\partial n_s} = \frac{\beta V^E}{n_a+n_b}\frac{\partial P}{\partial n_s} - \frac{n_s}{n_a+n_b}\frac{\partial \ln\gamma_s}{\partial n_s} + \frac{x_b}{n_a+n_b}\left[C_{bs} - C_{as}\right] \qquad (T,\ V\ constant) \quad (3.8b)$$

Eqs.(3.8) are combinations of the GD and the affinity relations expressing the activity of solvent a in terms of the solvent affinity and the salt activity. If we have a theory for the salt activity γ_s, which we do, i.e., the MSA, we can integrate (3.9) to obtain the solvent activity γ_a. This constitutes a workable algorithm for obtaining the solvent activities. We note that the GD equation alone is not complete. For ternary mixtures, we need two more equations for solvability. From eq.(3.8), we need supply (i) the salt activity coefficient and (ii) the KB affinity (or equivalents) or the excess volumes.

A further note on the derivation of (3.8). It can be easily generalized to higher component systems, e.g., $a+b+c+\cdots+s$. By repeated use of the affinity relations (3.7) between ab, ac, ... pairs, one can eliminate all cosolvent activities (after introducing the affinity (3.3b)) except for solvent a. A similar equation like (3.9a) will result (constant T,P):

$$\frac{\partial \ln\gamma_a}{\partial n_s} = -\frac{n_s}{n_a+n_b+n_c}\frac{\partial \ln\gamma_s}{\partial n_s} + \qquad (3.9)$$
$$+\frac{x_b}{n_a+n_b+n_c}\left(C_{bs} - C_{as} + \frac{\rho\bar{V}_s(\bar{V}_b - \bar{V}_a)}{kTK_T}\right) + \frac{x_c}{n_a+n_b+n_c}\left(C_{cs} - C_{as} + \frac{\rho\bar{V}_s(\bar{V}_c - \bar{V}_a)}{kTK_T}\right)$$

These equations can be numerically integrated from salt concentration $x_s = 0$ to the given x_s at constant system temperature T_0.

IV. Application to alcohol-water-salt solutions

Two mixtures (1) methanol + water + LiBr and (2) methanol + water + LiCl are examined as examples. These systems are selected due their importance as working fluids in absorption refrigeration applications. However, neither the partial molar volumes nor the DCFI's in these mixtures are available from experiments. Raatschen 1985 reported some density information. That leaves the DCFI's. The experimental determination of Kirkwood-Buff quantities are slowly gaining attention in the literature (Lepori and Matteoli 1984, Wooley and O'Connell 1991, Rubio et al. 1986, Pool 1962, Hamad and Mansoori 1990). Although the data base is being built up, few exist for our working fluids. To keep within engineering application, we make an empirical fit of the affinities from the VLE data at hand. This will not become a "circular" exercise, in that the Gibbs-Duhem equation for ternary mixtures needs two outside inputs to be closed: here a salt activity, and a solvent affinity.

VLE data are available from (1) methanol (a) + water (b)+ LiBr (s) (Raatschen 1985) and (2) methanol (a) + water (b) + LiCl (s) (Broul et al. 1969). We estimated the affinity relations from these data. Note that integrating (3.3b) gives (with unit fugacity coefficients, $\phi_i \approx 1$)

$$\int_{n_s=0}^{n_s} dn_s \left[\frac{\partial \ln\gamma_a}{\partial n_s} - \frac{\partial \ln\gamma_b}{\partial n_s} \right]_{T,P,N_{k\neq s}} = \ln\left(\frac{\gamma_a/\gamma_b}{\gamma_a^0/\gamma_b^0} \right) = \ln\left(\frac{\alpha_s}{\alpha_0} \right) \approx k_F x_s \tag{4.1}$$

For k_F, we found that it is not a constant in relation to x_s as proposed by Furter, especially at high salt concentrations. Figures 1 and 2 show the curves $\ln(\alpha_s/\alpha_0)$ vs x_s for the two cases (using experimental data only). Clearly, the curves are nonlinear starting at

$x_s \sim 0.06$.. Thus we propose the empirical modifications:

For Methanol (a) + water (b) + LiBr (s)

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = 5x_s - (x_a^0 - 0.34662)x_s(1 + x_s)^{17.175}, \qquad (at\ 40°C) \tag{4.2}$$

For Methanol (a) + water (b) + LiCl (s)

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = 5x_s - (x_a^0 - 0.35)(1.588 - x_a^0)x_s(1 + x_s)^{13.173}, \qquad (at\ 60°C) \tag{4.3}$$

(Note that (4.3) is improved over Wu and Lee 1992). These affinity formulas reproduce the vapor-liquid equilibrium data of Raatschen (1985) and Broul et al. (1969). During the integration, the solvent/cosolvent ratio (x_a/x_b) was kept constant, and the temperature was also kept constant. Pressure is allowed to vary when equilibrium is reached. Then there is a pressure effect. However, we estimate the term $V^E P/RT$ is to ber less than 0.00003 over the entire integration range. The magnitude of $\ln\gamma_a$ depending on the mixture concentration is around -0.2 to -0.5. Thus we can ignore the pressure term in our computer calculation.

For the salt activity coefficients γ_s, we used the MSA formulas as in Wu and Lee (1992). (Readers can refer to this reference for details.) Then eq.(3.9) was used to numerically integrate for the solvent activities γ_a and γ_b. The total pressure of the system was obtained from

$$P = x_a\gamma_a P_a^\sigma + x_b\gamma_b P_b^\sigma \tag{4.4}$$

where P_a^σ is the vapor pressure of a at T_0. The vapor phase composition y_a was then

given by

$$y_a = x_a \gamma_a P_a^{\sigma} / P \tag{4.5}$$

To fit the MSA activity coefficient γ_s to the data, we allowed the average "ion-pairing distance": the distance between cations and anions, to vary with the salt concentration, as well as the n_a/n_b ratio. (These are the only adjustible parameters in the fitting.) If we keep the anion diameter at the Pauling crystalline value (e.g., for σ_{Cl^-}, we used 3.62 Å), then the difference is made up by a pseudo-cation diameter, σ_+, inclusive of the radii of the cation and the intervening (*solvating*) solvent diameters.

Table 1 shows the results for the methanol-water-LiBr case. Table 2 shows the results for the methanol-water-LiCl case. It is seen that the total pressure can be accurately predicted. The vapor phase mole fractions are also reasonably well predicted. Figure 3 shows the P-x-y diagram for the methanol-water-LiCl system. The total pressure of the system is consistently lowered as the concentration of salt LiCl is increased. The x-y plot of Figure 4 is instructive in showing the salting-out behavior. The vapor phase is enriched with methanol (the component been salted out) as LiCl is added, although the total pressure of the system is uniformly depressed (namely, the depression of water vapor pressure is greater than the depression of the methanol vapor pressure, thus causing a "relative" enrichment of methanol in the vapor phase). Since water has higher affinity with LiCl, water prefers to stay in the liquid phase.

Figure 5 shows the variation of the pseudo-ion diameter (or rather the size of the solvated ionic sphere: ion plus its solvation shells) of the Li^+ ion in the methanol-water-LiCl system as a function of salt concentration and solvent/cosolvent ratio. It is seen that higher

LiCl x_s "diminishes" the ion-pairing distances. This is consistent with our reasoning above. As the methanol concentration increases, the solvated ion size also increases. This is again consistent. While we do not claim that our distances, which are dependent on the theories employed, are the "true" ones, they are consistent with experimental information.

V. Conclusions

We have derived a general and exact solvent affinity formula for mixed-solvent electrolyte solutions based on molecular principles (the Kirkwood-Buff theory of solutions*). We showed that the conventional Setchenov and Furter principles of "salting-out" in electrolyte solutions are special cases of the general formula (3.3). Knowing this general formula, it will facilitate future studies in salting-out behavior (1) by providing a standard, and (2) by encouraging data acquisition for testing.

In applications, we have tested the Gibbs-Duhem algorithm for two ternary salt systems: methanol-water-LiBr and methanol-water-LiCl by using an empirical affinity principle. This approach is designed not only for ternary but also for higher-component systems. For the ion activities, we used the mean-spherical approximation (MSA) of statistical mechanics. We have shown elsewhere (Landis 1985) that the MSA is sufficiently accurate for concentrated electrolyte solutions. The present approach offers an alternative to the free energy based models of electrolytes.

---

* In using the Kirkwood-Buff theory for electrolyte solutions, one should be careful in treating the "divergences" of the Kirkwood factors. See Kusalik and Patey 1987. By employing their methods, these indeterminacies can be removed.

References:

Blum, L. and Høye, J. 1977. Mean spherical model for asymmetric electrolytes. 2. Thermodynamic properties and the pair correlation function. J. Phys. Chem. **81**: 1311-1316.

Broul, M., Hlavaty, K., and Linek, J. 1969. Liquid-vapor equilibrium in systems of electrolytic components V. The system methanol-water-LiCl at 60°C. Collec. Czech. Chem. Commun. 34: 3428-3435.

Debye, P. and H Theory of electrolytes. I. Freezing point lowering and related phenomena. Z. Physik **24**: 185.

Fuoss, R.M. 1934 Distribution of ions in electrolytic solutions. Trans. Faraday Soc. **30**: 967-980.

Furter W.F. and Cook R.A. 1967. Salt effect in distillation: a literature review. *,Int'l J. Heat Transfer* **10**, 23-33.

Furter, W.F. 1972, Extractive distillation by salt effect. ACS Symposium Series #155: 35-45.

Harvey, A.H. and Prausnitz, J.M. 1989. Thermodynamics of high-pressure aqueous systems containing gases and salts. AIChE J 35: 635-644.

Hamad, E.Z. and Mansoori, G.A. 1990. Model calculations of thermodynamic mixture properties from direct correlation integrals. Z. Phys. Chem. N.F. **166**: 63-69.

Johnson, A.I. and Furter, W.F. 1960. Salt effect in vapor-liquid equilibrium, Part II. Can. J. Chem. Eng. 38: 78-87.

Kirkwood, J.G. and Buff, F.P. 1951. The statistical mechanics theory of solutions. J.Chem.Phys. **19**: 774.

Kolker, A. and de Pablo, J.J., 1995a. Thermodynamic modeling of concentrated aqueous electrolyte and nonelectrolyte solutions. AIChE J. **41**: 1563-1571.

Kolker, A. and de Pablo, J.J., 1995b. Thermodynamic modeling of concentrated multicomponent aqueous electrolyte and nonelectrolyte solutions. Chem. Eng. Sci. **50**: 1953-1959.

Kusalik, P.G. and Patey, G.N. 1987. The thermodynamic properties of electrolyte solutions: Some formal results. J. Chem. Phys. 86: 5110-5116.

Kolker, A. and de Pablo, J.J., 1996. Thermodynamic modeling of vapor-liquid equilibria in mixed aqueous-organic systems with salts. Ind. Eng. Chem. Res. **35**: 234-240.

Landis, L.H. 1985. Mixed-salt electrolyte solutions: accurate correlations for osmotic coefficients based on molecular distribution functions. Ph.D. Dissertation, University of Oklahoma.

Lane, M.J. and Huey, M.A., 1995, July. Lithium bromide absorption chiller passes gas conditioning field test. Oil & Gas J. 70-74.

Lee, L.L., Debenedetti, P.G. and Cochran, H.D. 1991. Fluctuation theory of supercritical solutions. in "Supercritical Fluid Technology", edited by Bruno, T.J and Ely, J.F. CRC Press, Boca Raton, Chapter 4, 193-226.

Lee, L. L., Chapman, W. G., Llano-Restrepo M., Shukla, K.P., 1996. Improved MSA theory for concentrated ionic solutions based on the Monte Carlo simulation at high ionic strengths. J. ChIChE, July 1996.

Long, F.A. and McDevit, W.F., 1952. Activity coefficients of nonelectrolyte solutes in aqueous salt solutions. Chem. Rev. 51:119-169.

Macedo, E.A., Skovborg, P, and Rassmussen, P. 1990. Calculation of phase equilibria for solutions of strong electrolytes in solvent-water mixtures. Chem. Eng. Sci. **45**: 875-882.

Marcus, Y. 1985. "Ion Solvation" (Wiley-Interscience, Chichester) pp. 117-120.

Matteoli, E. and Lepori, L. 1984 Solute-solute interactions in water II. Analysis through the Kirkwood-Buff integrals for 14 organic solutes. J. Chem. Phys. **80**: 2856-2863.

Morita, T. 1958. Theory of classical fluids: Hypernetted chain approximation, I. Progr. Theor. Phys. **20**: 920-938.

Neilson, G.W. and Enderby, J.E. 1979. Ann. Rep. Prog. Chem. Sect. C **76**: 185.

Newsome, J.R., Neilson, G.W., and Enderby, J.E., 1980. J. Phys. C **13**,: L923.

O'Connell, J.P., 1990. in "*Fluctuation theory of mixtures"*, edited by E. Matteoli and G.A. Mansoori (Taylor & Francis, New York), pp.45-67.

Pawlikowski, E.M. and Prausnitz, J.M. 1983. Estimation of Setchenov constants for nonpolar gases in common salts at moderate temperatures. Ind. Eng. Chem. Fundam. 22: 86-90.

Pitzer, K.S., 1973. Thermodynamics of electrolytes I: theoretical basis and general equations. J. Phys. Chem. **77**: 268.

Platford, R.F. 1979 in "Activity coefficients in electrolyte solutions", edited by Pytkowicz, R.M., CRC Press, Boca Raton, Florida, Chapter 3: 65.

Pool, R.A.H., Saville, G., Herrington, T.M., Shields, B.D.C., and Staveley, L.A.K. 1962 Some excess thermodynamic functions for the liquid systems argon+oxygen, argon+nitrogen, nitrogen+oxygen, nitrogen+CO, and argon+CO. J. Chem. Soc. Faraday Trans. **58**:

1962-1704.

Raatschen, W. 1985. Thermophysikalische Eigenschaften von Methanol-Wasser-Lithiumbromid Lösungen, Doktor-Ingenieurs Dissertation, Aachen.

Raatschen, W., Harvey, A.H., and Prausnitz, J.M. 1987. Equation of state for solutions of electrolytes in mixed solvents. Fluid Phase Equil. **38**:19-38.

Rubio, R.G., Prolongo, M.G., Cabrerizo, U, Diaz Pena, M, and Renuncio, J.A.R., 1986 Kirkwood-Buff integrals in non-electrolyte solutions. An evaluation of the local composition from experimental data. Fluid Phase Equil. **26**: 1-13.

Setchenov, J., 1889, Ueber die Konstitution der Salzlösungen auf Grund ihres Verhaltens zu Kohlensäure. Z. Phys. Chem. **4**: 117-125.

Stillinger, F. H. and Lovett, R. 1968. Ion pair theory of concentrated electrolytes. I. Basic Concepts and II. Approximate dielectric response calculation. J. Chem. Phys. **48**, 3858-3884.

Walters, H., Brooks, D.E., Fisher, D. 1985. editors. "Partitioning in aqueous two-phase systems." Academic Press, London.

Weingaertner, D.A., Lynn, S., and Hanson, D.N. 1991. Extractive crystallization of salt from concentrated aqueous solution. Ind. Eng. Chem. Res. 30: 490-501.

Wooley, R.J. and O'Connell, J.P. 1991 A database of fluctuation thermodynamic properties and molecular correlation function integrals for a variety of binary liquids. Fluid Phase Equil **66**: 233-261.

Wu, R.S and Lee, L.L. 1992 Vapor-liquid equilibria of mixed-solvent electrolyte solutions:

ion size effects based on the MSA theory. Fluid Phase Equil. 78: 1-24.

Yamagami, M, Wakita, H., and Yamaguchi, T., 1995. Neutron diffraction study of chloride ion solvation in water, methanol, and N,N-dimethylformamide. J. Chem, Phys. **103**: 8174-8178.

Zerres, H., and Prausnitz, J.M. 1994. Thermodynamics of phase equilibria in aqueous-organic systems with salt. AIChE J. **40**:676-691.

Table 1. Vapor-Liquid Equilibria for Methanol (a)-Water (b)-LiBr (s): at T= 40°C. Data from Raatschen 1985. Calculation via eq.(3.9a).

x_a^0	x_s	x_a	y_a (exp)	y_a (cal)	*P mmHg (exp)*	*P mmHg (cal)*	σ_{Li+}*
0.0504	*0.1189*	*0.0444*	*0.4767*	*0.4986*	*52.3*	*52.4*	*2.53*
0.0596	*0.1545*	*0.0504*	*0.4544*	*0.6500*	*34.2*	*34.5*	*2.33*
0.6160	*0.0750*	*0.5700*	*0.87*	*0.90*	*128.2*	*127.2*	*6.26*
0.6350	*0.1213*	*0.5580*	*0.9073*	*0.9103*	*122.6*	*122.9*	*3.89*
0.8610	*0.0855*	*0.7870*	*0.9550*	*0.9629*	*203.0*	*203.4*	*3.56*
0.8710	*0.1350*	*0.75*	*0.9580*	*0.9573*	*131.3*	*131.4*	*3.77*

*σ_{Li+} is the part of the ion-pairing distance (between a cation and its partner anion mediated through the solvent molecules: SSHIP or SSIP) attributed to the cation Li^+. (The anion size is fixed arbitrarily at 3.62 Å.)

Table 2. Vapor-Liquid Equilibria for Methanol (a)-Water (b)-LiCl (s): at T= 60°C. Data from Broul et al. 1969. Calculation by (3.9a).

x_a^0	x_s	x_a	y_a (exp)	y_a (cal)	*P mmHg (exp)*	*P mmHg (cal)*	σ_{Li+}
0.0076	*0.0296*	*0.0074*	*0.0418*	*0.0720*	*144.7*	*144.7*	*6.16*
0.0079	*0.1476*	*0.0067*	*0.1144*	*0.1347*	*77.86*	*77.89*	*3.47*
0.0057	*0.1568*	*0.0048*	*0.0926*	*0.1064*	*69.87*	*69.33*	*3.40*
0.1185	*0.0062*	*0.1178*	*0.4896*	*0.4946*	*258.8*	*258.9*	*8.46*
0.1113	*0.0325*	*0.1077*	*0.4989*	*0.5152*	*245.1*	*245.2*	*6.40*
0.1240	*0.0827*	*0.1137*	*0.5880*	*0.6058*	*233.9*	*233.7*	*4.67*
0.1145	*0.2174*	*0.0879*	*0.7249*	*0.7487*	*101.0*	*101.3*	*3.41*
0.3874	*0.0134*	*0.3822*	*0.7522*	*0.7590*	*401.5*	*401.6*	*9.60*
0.3580	*0.0439*	*0.3423*	*0.7607*	*0.7482*	*378.7*	*378.6*	*6.74*
0.3564	*0.0697*	*0.3316*	*0.7761*	*0.7923*	*359.6*	*359.1*	*6.06*
0.3383	*0.1826*	*0.2765*	*0.8488*	*0.8644*	*189.3*	*189.9*	*4.59*
0.6040	*0.0147*	*0.5951*	*0.8465*	*0.8540*	*476.9*	*476.6*	*13.15*
0.6109	*0.0733*	*0.5661*	*0.8759*	*0.8847*	*422.5*	*422.9*	*7.70*
0.6101	*0.1316*	*0.5298*	*0.8996*	*0.9118*	*311.4*	*311.7*	*6.54*

Figure Captions

Figure 1.: The relative volatility ratio as a function of salt mole fraction x_s for the methanol (a) + water (b) + LiBr (s) system at 40°C. Symbols: experimental data of Raatschen (1985). Line: the present correlation, eq.(4.3) x^0_{MeOH} is the mole fraction of methanol in the clean solution. Each line is at the same solvent/cosolvent n_a/n_b ratio. The spread of x^0_{MeOH} (e.g. from 0.052 to 0.055) derived from the data source (given as is).

Figure 2.: The relative volatility ratio as a function of salt mole fraction x_s for the methanol (a) + water (b) + LiCl (s) system at 60°C. Symbols: experimental data of Broul et al. (1969). Line: the present correlation, eq.(4.2)

Figure 3.: The P-x-y diagram for the methanol (a) + water (b) + LiCl (s) system at 60°C. Symbols: experimental data of Broul et al. (1969). Line: the present solution, eq.(3.9a)

Figure 4.: The x-y diagram for the methanol (a) + water (b) + LiCl (s) system at 60°C. Symbols: experimental data of Broul et al. (1969). Line: the present solution, eq.(3.9a). Note that with addition of salt (LiCl), the methanol escapes to the vapor phase, salted-out.

Figure 5.: The part of the solvent-averaged ion-pairing distance that is attributed to the cation Li^+ (anion size is chosen to be 3.62 A) for methanol (a) + water (b) + LiCl (s) system at 60°C. Increasing salt mole fraction means less shared solvent molecules. For each isopleth (fixed x^0_{MeOH}), the ion-pairing distance shrinks with added salt x_s. Higher methanol content also implies larger solvation diameter (a molecule of methanol is bulkier than water).

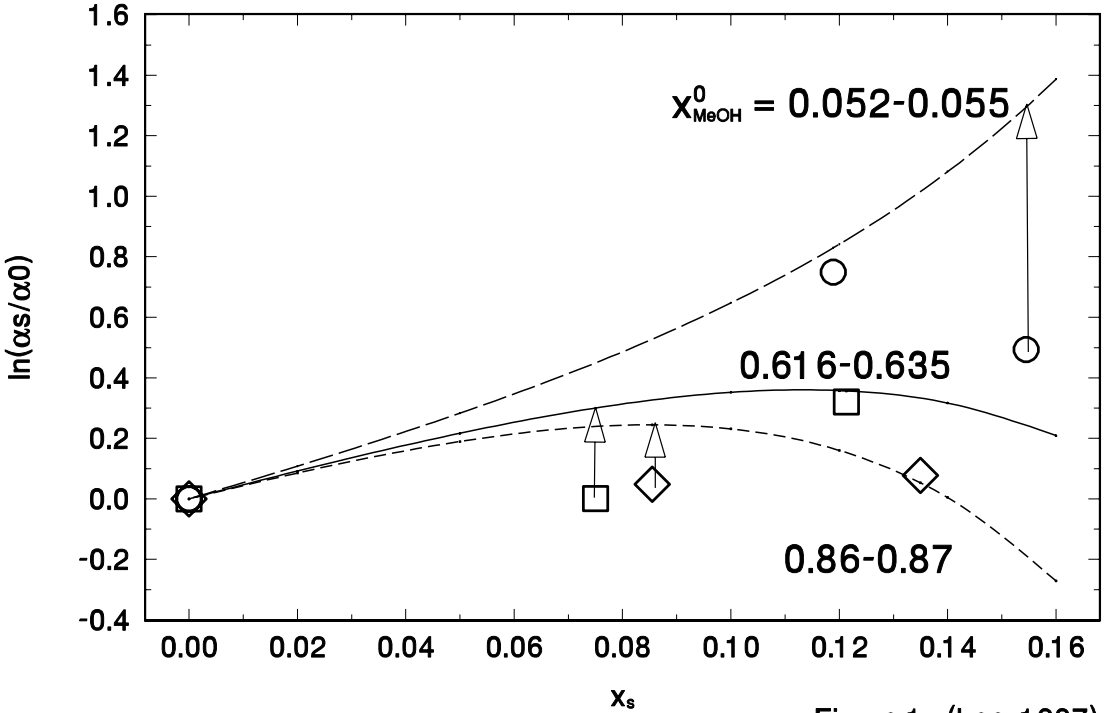

Figure 1. (Lee, 1997)

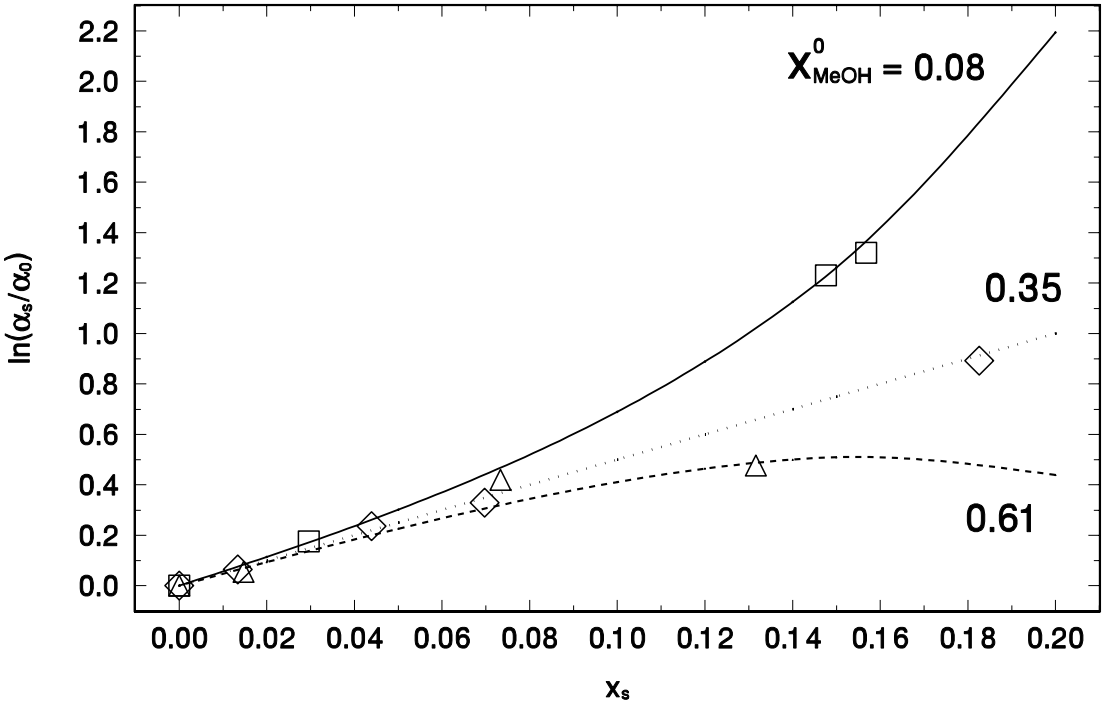

Figure 2. (Lee, 1997)

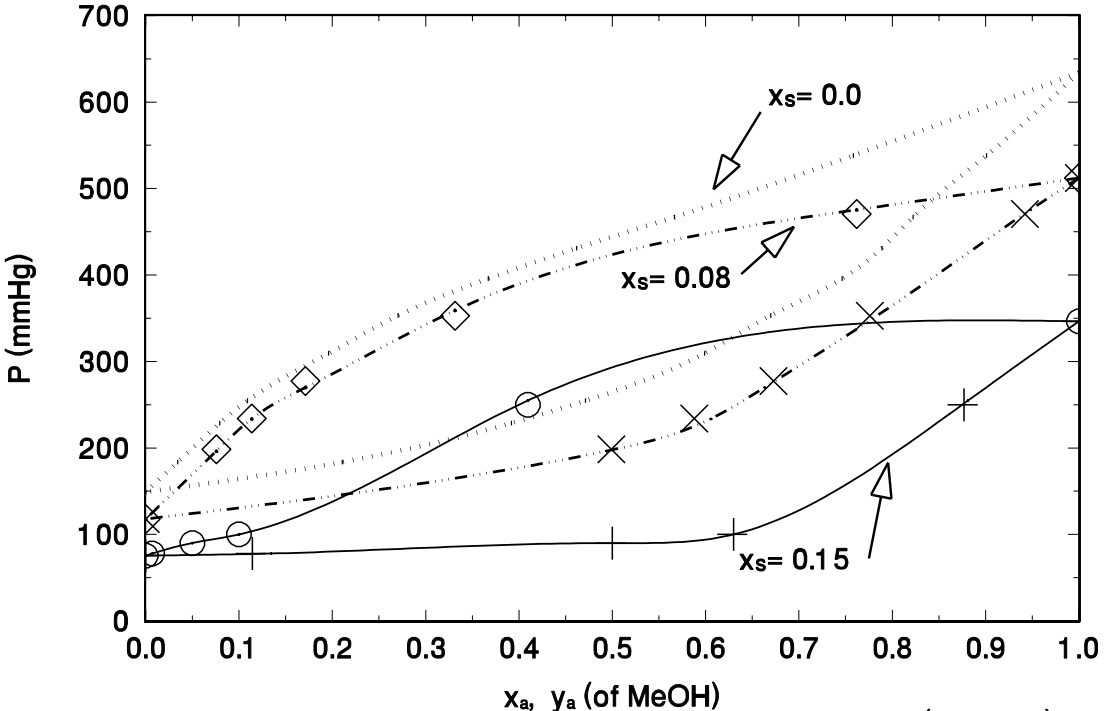

Figure 3. (Lee, 1997)

XYMOHCL Apr. 28, 1997 1:02:35 AM

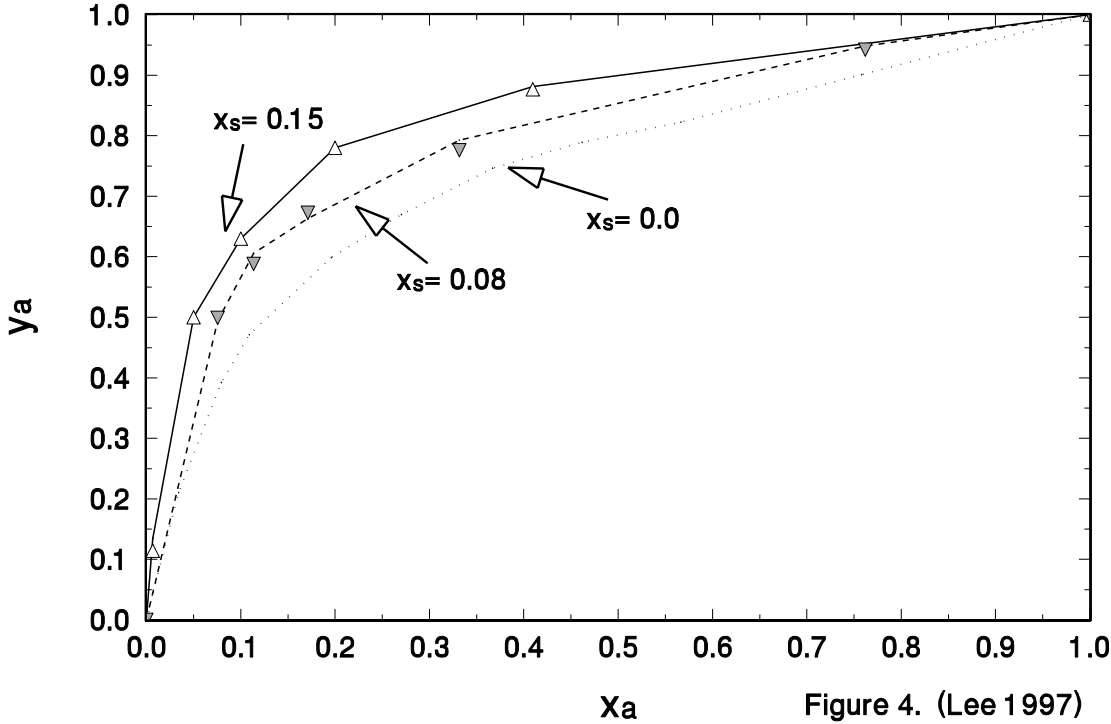

Figure 4. (Lee 1997)

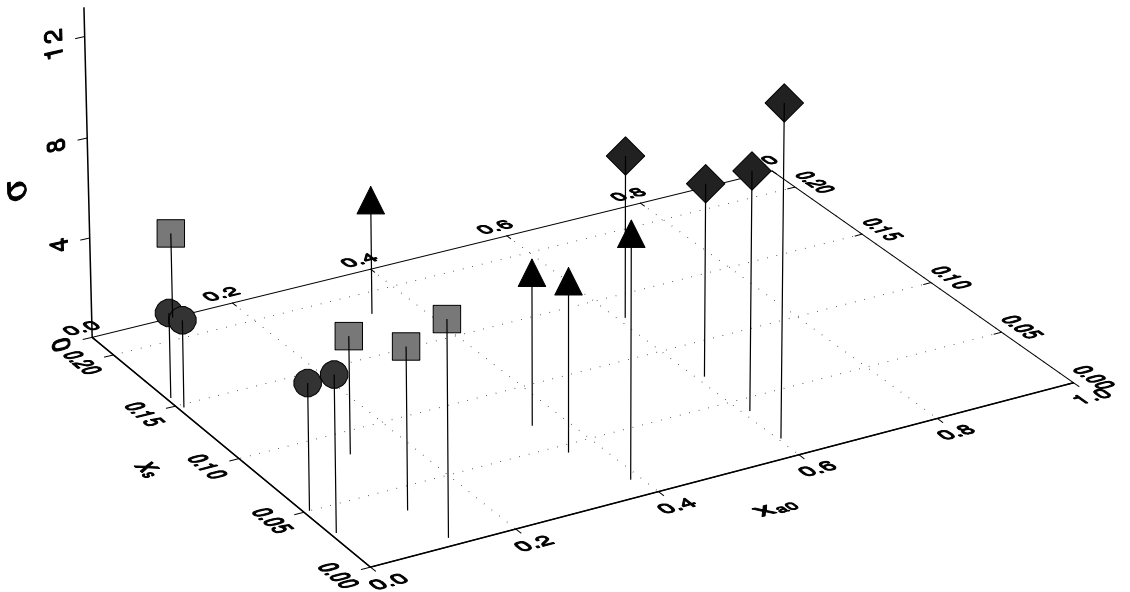

Figure 5 (Lee, 1997)