Relations Among Concentration Fluctuation Integrals in Mixtures
(Theory and Experiments)

Esam Z. Hamad and G.Ali Mansoori
University of Illinois at Chicago, (M/C 063), Chicago, IL 60607-7052, USA

Enrico Matteoli and Luciano Lepori
Istituto di Chimica del CNR,
Via Risorgimento 35, 56100 Pisa, Italy

Liquid binary mixtures / Concentration fluctuation theory / Fluctuation integral data / Tetrachlormethane-organic fluids / Water-organic fluids

Based on a mathematical consistency condition, new relations among the concentration fluctuation integrals in mixtures are derived. These relations indicate that for a binary mixture only one of the fluctuation integrals is independent. A closure procedure is proposed to relate $G_{11}$ and $G_{22}$ to $G_{12}$ in order to obtain analytic expressions for fluctuation integrals and the related direct correlation integrals.

New experimental fluctuation integral data for binary mixtures of tetrachloromethane with six organic fluids (methanol, ethanol, propanol, n-butanol, tetrahydrofuran, and 1,4-dioxane), water + methanol at different temperatures and water + ethanol at different temperatures are reported. The new data and the binary data of water with ten organic fluids (acetone, acetonitrile, 2-aminoethanol, dimethylsulfoxide, methanol, ethanol, propanol, tert-butanol, tetrahydrofuran, and 1,4-dioxane) are used to test the validity of the proposed theory. Considering the limitations of the closure procedure and the accuracy of the experimental data it is shown that the theory is in agreement with the data.

Aufgrund einer mathematischen Konsistenzbedingung werden neue Beziehungen zwischen den Fluktuationsintegralen der Konzentrationen in Mischungen abgeleitet. Diese Beziehungen zeigen, daß für binäre Mischungen nur eines der Fluktuationsintegrale unabhängig ist. Für die Verknüpfung von $G_{11}$ und $G_{22}$ mit $G_{12}$ wird ein als „closure approximation“ bezeichnetes Verfahren vorgeschlagen, um analytische Ausdrücke für Fluktuationsintegrale und die verwandten direkten Korrelationsintegrale zu erhalten.

Authors email addresses:
E.Z. Hamad (esam.hamad@aramcoservices.com); G.A. Mansoori (mansoori@uic.edu);
E. Matteoli (matteoli@ipcf.cnr.it), L. Lepori (lepori@ipcf.cnr.it)
Neue experimentelle Werte der Fluktuationsintegrale binärer Mischungen bei verschiedenen Temperaturen werden mitgeteilt, und zwar von Tetrachlormethan mit sechs organischen Flüssigkeiten (Methanol, Ethanol, Propanol, n-Butanol, Tetrahydrofuran und 1,4-Dioxan) sowie von Wasser-Methanol und Wasser-Ethanol. Die neuen Werte und die binären Daten von Wasser mit zehn organischen Flüssigkeiten (Aceton, Acetonitril, 2-Aminoethanol, Dimethylsulfoxid, Methanol, Ethanol, Propanol, tert-Butanol, Tetrahydrofuran und 1,4-Dioxan) werden herangezogen, um die Gültigkeit der vorgeschlagenen Theorie zu prüfen. In Anbetracht der Grenzen des benutzten Verfahrens und der Genauigkeit der experimentellen Daten steht die Theorie in Einklang mit den Meßwerten.

Introduction

Studies in concentration fluctuations in mixtures have resulted in numerous advances in the fundamental understanding of behaviour of mixtures at, and away from, equilibrium [1–3]. Definition of properties of mixtures in terms of concentration fluctuations has always been a viable empirical and theoretical route for analysis, correlation and prediction of mixture properties [4–8]. The empirical concept of “local compositions” is recently linked to the theory of concentration fluctuations [5]. Combination of the conformal solution theory and concentration fluctuation theory have resulted in new mixing rules which have found special utility for asymmetric mixtures of interest in high pressure supercritical extraction phenomena.

Among the concentration fluctuation theories of statistical mechanics the Kirkwood-Buff solution theory [4] is the one which is developed specifically for mixtures at equilibrium [4]. This theory is found to be quite useful in analysis and prediction of properties of asymmetric and/or highly polar mixtures for which there is limited or no knowledge about their intermolecular potential energy functions [2, 3]. The basic relation of the Kirkwood-Buff solution theory is derived using the grand canonical ensemble theory and it is as follows [4]:

\[ kT \langle \frac{\partial \langle N_i \rangle}{\partial \mu_j} \rangle_{V, N, T, \delta_{ij}} = \langle N_i \rangle \langle N_j \rangle G_{ij} V + \delta_{ij} \langle N_i \rangle. \]  

(1)

In this expression \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( V \) is the total volume, \( \langle N_i \rangle \) is the average number of particles of type \( i \) in the grand canonical ensemble, \( \mu_j \) is the chemical potential of component \( j \), \( \delta_{ij} \) is the Kroneker delta and \( G_{ij} \) is the Kirkwood-Buff integral defined by the following expression:

\[ G_{ij} = \int_{V} \left[ g_{ij}(r) - 1 \right] dr \]  

(2)

where \( g_{ij}(r) \) is the radial distribution function of molecules of type \( j \) around a central molecule of type \( i \) and \( g_{ij}(r) = g_{ji}(r) \). Provided that information is available about \( G_{ij} \) integrals, defined by Eq. (2), Eq. (1) can be used to calculate chemical potentials of components of a mixture. Also the information about \( G_{ij} \) can provide us with the means of calculating other
Relations Among Concentration Fluctuation Integrals in Mixtures

properties of a mixture such as the isothermal compressibility \( \kappa \), and the partial molar volumes, \( v_i \), by the following expressions:

\[
(\rho k T \kappa)^{-1} = \rho \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j |B_{ij}|/|B|, \quad (3)
\]

\[
\rho v_i = \sum_{j=1}^{c} x_j |B_{ij}| / \sum_{j=1}^{c} \sum_{k=1}^{c} x_j x_k |B|_{jk}, \quad (4)
\]

where \( c \) is the number of components in the mixture, \( B \) is a \( c \times c \) matrix with elements, \( B_{ij} \), defined by

\[
B_{ij} = \rho x_i [\delta_{ij} + x_j \rho G_{ij}], \quad (5)
\]

\( x_i \) is the mole fraction of component \( i \), \( |B|_{ij} \) is the cofactor of the element \( B_{ij} \), and \( |B| \) is the determinant of the matrix \( B \).

Expansions of the \( G_{ij} \)'s in powers of concentration are available [19, 20]. However, the coefficients in these expansions are given in terms of third, fourth and higher order correlation functions. Since little is known about correlation functions of order higher than two, the expansions are in the time being of limited practical use.

Theoretical calculation of \( G_{ij} \) integrals requires the knowledge about the radial distribution functions, \( g_{ij} \). The radial distribution functions can generally be calculated using the theory of intermolecular potential energy functions in the context of a partition function. However, for complex mixtures, mixtures consisting of asymmetric molecules or highly polar and associating molecules, the intermolecular potential energy functions are not well known. Also the existing techniques of calculating radial distribution functions from the knowledge of intermolecular potential energy functions require extensive numerical calculations [9]. In the present report it is shown that not all the \( G_{ij} \)'s are independent; only one of them is independent regardless of the number of components in the mixture. A technique is then presented through which we have been able to develop expressions for calculation of \( G_{ij} \) integrals without the need for the knowing of radial distribution functions. We have also performed indirect measurements of \( G_{ij} \) integrals and we have made comparisons between the measurements and the theoretical technique of calculating \( G_{ij} \)'s.

**Theory of calculating \( G_{ij} \)'s**

In what follows we present the technique for calculating \( G_{ij} \) for binary mixtures. Extension of this technique to multicomponent mixtures is straightforward. Eq. (1) can be reformulated in terms of the direct correlation integrals, \( C_{ij} \), defined by

\[
C_{ij} = \int c_{ij}(r)dr. \quad (6)
\]
In the above equation $c_{ij}(r)$ is the direct correlation function, which is related to the radial distribution function through the following expression [10, 18]

$$c_{ij}(r_{12}) = h_{ij}(r_{12}) - \sum_{k=1}^{c} \varrho_k \int c_{ik}(r_{13})h_{jk}(r_{23})dr_3,$$

where

$$h_{ij}(r) = g_{ij}(r) - 1$$

and $\varrho_k = \varrho x_k$. In terms of the direct correlation integrals the isothermal compressibility and the partial molar volume become [10, 18]:

$$(\varrho kT\kappa)^{-1} = 1 - \varrho \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j C_{ij},$$

$$\varrho v_i = \left(1 - \varrho \sum_{j=1}^{c} x_j C_{ij}\right)\left(1 - \varrho \sum_{j=1}^{c} \sum_{k=1}^{c} x_j x_k C_{jk}\right).$$

For binary mixtures the relation between the chemical potential and the direct correlation integrals is [10, 18]:

$$x_i[\partial \mu_i/\partial x_i]_{p,T} = kT \frac{1 - x_1 \varrho C_{11} - x_2 \varrho C_{22} + x_1 x_2 \varrho^2 (C_{11}C_{22} - C_{12}^2)}{1 - \varrho \sum x_i x_j \varrho C_{ij}}.$$  

$$q_{G_{1i}} = \frac{x_i \varrho C_{1i} - (1 - x_i) \varrho^2 (C_{11}C_{22} - C_{12}^2)}{1 - x_1 \varrho C_{11} - x_2 \varrho C_{22} + x_1 x_2 \varrho^2 (C_{11}C_{22} - C_{12}^2)}, i = 1,2$$

$$q_{G_{12}} = \frac{x_1 \varrho C_{12}}{1 - x_1 \varrho C_{11} - x_2 \varrho C_{22} + x_1 x_2 \varrho^2 (C_{11}C_{22} - C_{12}^2)}.$$  

To derive the relations among the $C_{ij}$ integrals we use the mathematical result that the mixed second derivatives of a function of two variables are equal at all points where the derivatives are continuous. For the chemical potential of component $i$ one has:

$$\partial^2 \mu_i/\partial x_i \partial p = \partial^2 \mu_i/\partial p \partial x_i, \quad i = 1,2.$$  

The derivative on the right-hand side of the above equation is equal to $\partial v_i/\partial x_i$. Eq. (14) now becomes

$$\partial^2 \mu_i/\partial x_i \partial p = \partial v_i/\partial x_i.$$  

Substituting the expressions for the partial molar volume and the chemical potential, Eqs. (10) and (11), in the above relation give:

\[
kT \frac{\partial}{\partial \ell} \left\{ \left[ 1 - x_1 \varphi C_{11} - x_2 \varphi C_{22} + x_1 x_2 \varphi^2 \right] (C_{11} C_{22} - C_{12}^2) \right\} \left/ \left[ 1 - \Sigma x_i x_j \varphi C_{ij} \right] \right\} \partial \ell = x_1 \frac{\partial}{\partial x_1} \left[ 1 - x_1 \varphi C_{11} - x_2 \varphi C_{12} \right] \left/ \varphi \left( 1 - \Sigma x_i x_j \varphi C_{ij} \right) \right\} \partial x_1
\]

(16)

and

\[
kT \frac{\partial}{\partial \ell} \left\{ \left[ 1 - x_1 \varphi C_{11} - x_2 \varphi C_{22} + x_1 x_2 \varphi^2 \right] (C_{11} C_{22} - C_{12}^2) \right\} \left/ \left[ 1 - \Sigma x_i x_j \varphi C_{ij} \right] \right\} \partial \ell = x_2 \frac{\partial}{\partial x_2} \left[ 1 - x_2 \varphi C_{22} - x_1 \varphi C_{12} \right] \left/ \varphi \left( 1 - \Sigma x_i x_j \varphi C_{ij} \right) \right\} \partial x_2.
\]

(17)

These two equations constitute two independent expressions relating \( C_{11}, C_{22} \) and \( C_{12} \) in a binary mixture. Other relations for different sets of independent variables have been derived in terms of both \( G_{ij} \)'s and \( C_{ij} \)'s; including those for multicomponent mixtures [11]. In principle Eqs. (16) and (17), together with another expression relating \( C_{12} \) to \( C_{11} \) and \( C_{22} \) can be used to solve for the three quantities. The expression relating \( C_{12} \) to \( C_{11} \) and \( C_{22} \),

\[
C_{12} = C_{12}(C_{11}, C_{22}; x_i, T, \ell)
\]

is not presently available in a general form. We will name Eq. (18) the “closure” expression. With an appropriate choice for the functional form for the closure expression, Eqs. (16)—(18) can be solved simultaneously for \( C_{11}, C_{22} \) and \( C_{12} \) and then for \( G_{11}, G_{22} \) and \( G_{12} \) using Eqs. (12) and (13).

**Choice of the closure expression for \( C_{12} \)**

Simultaneous solution of Eqs. (16)—(18) for \( C_{11}, C_{22} \) and \( C_{12} \) depends on the choice of closure expression for \( C_{12} \) in Eq. (18). Assuming that \( C_{12} \) is an average of \( C_{11}, C_{22} \), the simplest expressions which one can choose for Eq. (18) are:

1) geometric mean,

\[
C_{12} = \alpha (C_{11} C_{22})^{1/2},
\]

(19)

2) weighted arithmetic mean,

\[
C_{12} = \alpha C_{11} + \beta C_{22}
\]

(20)

or 3) a combination of both. In Eqs. (19) and (20) \( \alpha \) and \( \beta \) are adjustable parameters. The geometric mean does not always work for real fluids because, as shown elsewhere [11], \( C_{11} \) and \( C_{22} \) can have opposite signs.
Fig. 1. The linearity of $C_{12}/C_{11}$ versus $C_{22}/C_{11}$ for water + methanol and water + 2-aminoethanol binary mixtures.

Table 1. The deviations of direct correlation integrals from the relation $C_{12} = \alpha C_{11} + \beta C_{22}$.

<table>
<thead>
<tr>
<th>System</th>
<th>Temp. (°C)</th>
<th>$S^a \times 100$</th>
<th>Max. dev. $^b$ (%)</th>
<th>$x_1$ at Max. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water + methanol</td>
<td>0.0</td>
<td>0.96</td>
<td>7.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Water + methanol</td>
<td>25</td>
<td>0.34</td>
<td>-4.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Water + methanol</td>
<td>60</td>
<td>0.22</td>
<td>-2.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Water + ethanol</td>
<td>25</td>
<td>2.9</td>
<td>12</td>
<td>0.0</td>
</tr>
<tr>
<td>Water + ethanol</td>
<td>50</td>
<td>0.77</td>
<td>4.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Water + ethanol</td>
<td>90</td>
<td>1.3</td>
<td>6.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Water + propanol</td>
<td>25</td>
<td>0.43</td>
<td>-3.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Water + tert-butanol</td>
<td>25</td>
<td>0.42</td>
<td>-4.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Water + acetonitrile</td>
<td>25</td>
<td>2.3</td>
<td>-11</td>
<td>1.0</td>
</tr>
<tr>
<td>Water + acetone</td>
<td>25</td>
<td>1.5</td>
<td>-6.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Water + dimethylsulfoxide</td>
<td>25</td>
<td>0.57</td>
<td>-4.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Water + tetrahydrofuran</td>
<td>25</td>
<td>1.5</td>
<td>-7.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Water + 1,4-dioxane</td>
<td>25</td>
<td>1.3</td>
<td>-5.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Water + 2-aminoethanol</td>
<td>25</td>
<td>0.93</td>
<td>4.3</td>
<td>0.3</td>
</tr>
<tr>
<td>CCl$_4$ + methanol</td>
<td>25</td>
<td>0.10</td>
<td>-2.3</td>
<td>0.0</td>
</tr>
<tr>
<td>CCl$_4$ + ethanol</td>
<td>25</td>
<td>0.05</td>
<td>-1.5</td>
<td>0.0</td>
</tr>
<tr>
<td>CCl$_4$ + propanol</td>
<td>25</td>
<td>0.04</td>
<td>-1.5</td>
<td>0.0</td>
</tr>
<tr>
<td>CCl$_4$ + n-butanol</td>
<td>25</td>
<td>0.03</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CCl$_4$ + tetrahydrofuran</td>
<td>25</td>
<td>0.002</td>
<td>-0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>CCl$_4$ + 1,4-dioxane</td>
<td>25</td>
<td>0.0005</td>
<td>-0.1</td>
<td>0.6</td>
</tr>
</tbody>
</table>

$^a$ $S = \Sigma \{(C_{12,\text{pred.}} - C_{12,\text{exp.}})/C_{12,\text{exp.}}\}^2$.

$^b$ Dev. $= \{(C_{12,\text{pred.}} - C_{12,\text{exp.}})/C_{12,\text{exp.}}\} \times 100$. 
Relations Among Concentration Fluctuation Integrals in Mixtures

The validity of the weighted arithmetic mean can be verified by plotting \( C_{12}/C_{11} \) versus \( C_{22}/C_{11} \). The resulting curve should be linear according to Eq. (20). The \( C_{ij} \)'s for a number of binary mixtures are calculated using Eqs. (12) and (13), from the \( G_{ij} \)’s obtained in this work and from literature [12]. Fig. 1 shows the plot of \( C_{12}/C_{11} \) versus \( C_{22}/C_{11} \) for water + methanol and water + 2-aminoethanol binary mixtures. The linearity of the plot supports Eq. (20). Data for other binary mixtures are also compared to Eq. (20) and the maximum deviations are reported in Table 1. The maximum deviation for all studied systems is about 11%. Since some of the data has uncertainties up to 30–40% [12], one concludes that the weighted arithmetic mean is a good closure approximation.

To avoid having to solve numerically the nonlinear partial differential equations, Eqs. (16) and (17), one can make use of the fact that for liquids at low to moderate pressures the direct correlation integrals are weak functions of pressure. Under this assumption Eqs. (16) and (17) give:

\[
(1 - x_1q C_{11} - x_2q C_{12})/(q - q^2 \Sigma \Sigma x_j x_k C_{jk}) = v_1
\]  
(21)

\[
(1 - x_1q C_{12} - x_2q C_{22})/(q - q^2 \Sigma \Sigma x_j x_k C_{jk}) = v_2
\]  
(22)

where \( v_1 \) and \( v_2 \) are the molar volumes of pure components 1 and 2, respectively. Eqs. (21) and (22) imply that the partial molar volumes are equal to the pure component volumes at all concentrations. This is a direct result of assuming that the \( C_{ij} \)'s are pressure independent. This approximation, which is usually made in lattice models, does not have a pronounced effect on the \( C_{ij} \)'s as will be seen later. Joining Eqs. (21) and (22) with the equation for the isothermal compressibility, Eq. (9), gives:

\[
x_1q C_{11} + x_2q C_{12} = 1 + W[(v_1/v_2) x_1 + x_2]
\]  
(23)

\[
x_1q C_{12} + x_2q C_{22} = 1 + W[x_1(v_2/v_1)x_2]
\]  
(24)

where

\[
W = -[kT(x_1\kappa_1/v_2 + x_2\kappa_2/v_1)]^{-1}
\]  
(25)

and \( \kappa_1 \) and \( \kappa_2 \) are the isothermal compressibilities of the pure components.

The direct correlation integrals, \( C_{ij} \)'s, in a binary mixture can now be solved for by combining Eqs. (20), (23) and (24):

\[
q C_{11} = \frac{W(1 - \beta v_2/v_1)x_2^2 + Wx_1(\beta x_1 + x_2)v_1/v_2 + (1 - \beta)x_2 + \beta x_1}{\beta x_1^2 + x_1 x_2 + \alpha x_2^2}
\]  
(26)

\[
q C_{12} = \frac{W(\beta x_1^2 + \alpha x_1 x_2 v_1/v_2 + \beta x_1 x_2 v_2/v_1 + \alpha x_2^2) + \beta x_1 + \alpha x_2}{\beta x_1^2 + x_1 x_2 + \alpha x_2^2}
\]  
(27)

The integral \( C_{22} \) is obtained by interchanging \( \alpha \) and \( \beta \), and the subscripts 1 and 2 in the expression for \( C_{11} \). The \( G_{ij} \) integrals can be obtained from Eqs. (12) and (13).
Fig. 2. The variation of $\varrho G_{ij}$ with composition for TCM + methanol and for water + methanol [12]. The points represent the experimental data: $\varrho G_{11}$, $\varrho G_{12}$, and $\chi \varrho G_{22}$. The curves represent the model predictions: $\varrho G_{11}$, $\varrho G_{12}$, and $\varrho G_{22}$.

**Experimental data**

Previously two of the authors of this communication [12, 13] presented the experimental technique and some of the data which were produced for $G_{ij}$ integrals utilizing thermodynamic quantities such as activity coefficients, partial molar volumes and compressibilities of a number of water-organic mixtures. We have now determined the $G_{ij}$ values for mixtures of tetrachloromethane (TCM) with some of organic compounds which were studied in water-organic mixtures, namely: methanol, ethanol, 1-propanol, N-butanol, tetrahydrofuran (THF) and 1,4-dioxane. Simultaneous analysis of water-organic and TCM-organic data will enable us to demonstrate the
effect of various factors on $G_{ij}$ integrals, the role of hydrophobicity in association of solutes, the effect of composition change on $G_{ij}$'s, and validity of the closure expression for $C_{12}$.

The $G_{ij}$ integrals are expressed in terms of activity coefficients, $\gamma_i$, partial molar volume, $v_i$, and isothermal compressibility, $\kappa$, according to the following relations:

$$G_{12} = RT \kappa - v_1 v_2 / (vD)$$  \hspace{1cm} (28) \\
$$G_{it} = G_{12} + (v_j/D - v)/x_i, \hspace{1cm} t = 1, 2$$  \hspace{1cm} (29) \\

where $v$ is the molar volume of the mixture, $R$ is the universal gas constant and $D = x_i \frac{\partial \mu_i}{\partial x_i} |_{p,T}$. 

Fig. 3. The variation of $\rho G_{ij}$ with composition for TCM + ethanol and for water + ethanol [12]. For other details see caption to Fig. 2.
Inaccuracies in the quantity $D$ may cause up to $30-40\%$ uncertainty in $G_{ij}$, specially at their extrema with respect to composition. The standard deviation is not expected to be larger than $20\%$ in the dilute organic region ($x_1 > 0.95$) where abundant and more accurate data are available. However, such uncertainties will not affect the comparative study of $G_{ij}$ for different mixtures.

The sources of data for water + organic mixtures were quoted previously [12]. For TCM + organic mixtures activity coefficients and partial molar volume data were calculated from data measured at ICQEM-CNR.
Partial molal compressibility values were calculated from data of other investigators [15–17] or estimated from data of related compounds.

**Comparison and discussion**

Figs. 2–7 represent comparisons of $G_{ij}$ values for water + organic mixtures with TCM + organic mixtures. According to these figures, $G_{22}$ curves possess maxima and $G_{12}$ curves possess minima for large values of $x_1$ ($\sim 0.7 - 0.9$) where the organic compound is an alcohol. This behavior of
Fig. 6. The variation of $\phi G_{ij}$ with composition for TCM + tetrahydrofuran (THF) and for water + tetrahydrofuran [12]. For other details see caption to Fig. 2.

$G_{22}$ and $G_{12}$ curves is indicative of alcohol-alcohol association and lack of affinity of alcohol to water or TCM. In the water + organic systems the absolute value of extremum increase with increasing the hydrocarbon chain length of alcohols. In TCM + organic systems an opposite trend is observed.

The behavior of $G_{11}$ is particularly interesting: $G_{11}$ of TCM + alcohol systems has monotonic trend with increase of TCM concentration similar
Table 2. Molar volumes and isothermal compressibilities of the pure liquids used in this work.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>( v_i ) (cm(^3) mol(^{-1}))</th>
<th>( T (^\circ \text{C}) )</th>
<th>( \kappa_i \times 10^{-5}/\text{bar}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>18.07</td>
<td>0.0</td>
<td>5.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>4.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>4.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>4.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>4.68</td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>96.50</td>
<td>25</td>
<td>10.67</td>
</tr>
<tr>
<td>Methanol</td>
<td>40.73</td>
<td>0.0</td>
<td>10.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>12.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>15.70</td>
</tr>
<tr>
<td>Ethanol</td>
<td>58.68</td>
<td>25</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>18.0</td>
</tr>
<tr>
<td>Propanol</td>
<td>75.14</td>
<td>25</td>
<td>10.2</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>91.53</td>
<td>25</td>
<td>10.2</td>
</tr>
<tr>
<td>tert-Butanol</td>
<td>94.88</td>
<td>25</td>
<td>12.0</td>
</tr>
<tr>
<td>THF</td>
<td>91.53</td>
<td>25</td>
<td>10.2</td>
</tr>
<tr>
<td>DMSO</td>
<td>70.94</td>
<td>25</td>
<td>4.60</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>85.25</td>
<td>25</td>
<td>7.20</td>
</tr>
<tr>
<td>2-Aminoethanol</td>
<td>60.01</td>
<td>25</td>
<td>5.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>74.05</td>
<td>25</td>
<td>12.39</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>52.25</td>
<td>30</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Table 3. Values of the model-parameters \( \alpha \) and \( \beta \).

<table>
<thead>
<tr>
<th>Organic compound</th>
<th>( T (^\circ \text{C}) )</th>
<th>Water + organic</th>
<th>CCl(_4) + organic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \alpha )</td>
<td>( \beta )</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>Methanol</td>
<td>0</td>
<td>0.7633</td>
<td>0.3008</td>
</tr>
<tr>
<td>Methanol</td>
<td>25</td>
<td>0.4691</td>
<td>0.3577</td>
</tr>
<tr>
<td>Methanol</td>
<td>60</td>
<td>0.3890</td>
<td>0.3790</td>
</tr>
<tr>
<td>Ethanol</td>
<td>25</td>
<td>0.4672</td>
<td>0.2727</td>
</tr>
<tr>
<td>Ethanol</td>
<td>50</td>
<td>0.2268</td>
<td>0.3015</td>
</tr>
<tr>
<td>Ethanol</td>
<td>90</td>
<td>0.3494</td>
<td>0.3007</td>
</tr>
<tr>
<td>Propanol</td>
<td>25</td>
<td>0.2657</td>
<td>0.2382</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>25</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>tert-Butanol</td>
<td>25</td>
<td>0.2436</td>
<td>0.1891</td>
</tr>
<tr>
<td>THF</td>
<td>25</td>
<td>0.0749</td>
<td>0.2282</td>
</tr>
<tr>
<td>DMSO</td>
<td>25</td>
<td>2.4922</td>
<td>0.0932</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>25</td>
<td>0.0774</td>
<td>0.2105</td>
</tr>
<tr>
<td>2-Aminoethanol</td>
<td>25</td>
<td>1.1289</td>
<td>0.1912</td>
</tr>
<tr>
<td>Acetone</td>
<td>25</td>
<td>0.1203</td>
<td>0.2427</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>30</td>
<td>0.1885</td>
<td>0.3537</td>
</tr>
</tbody>
</table>
Fig. 7. The variation of $\varrho_{i1}$ with composition for TCM + 1,4-dioxane and for water + 1,4-dioxane [12]. For other details see caption to Fig. 2.

to the corresponding ideal solution case [12]. The $G_{11}$ functions of water show maxima for solutions of ethanol, propanol, and tert-butanol. Values at maxima of water are much larger than the corresponding maximum value of $G_{22}$. All this suggests that water plays an active role of association of hydrocarbon-like moieties, whereas in TCM the tendency to association of alcohols is to be ascribed to hydrogen bonding as expected.
Fig. 8. The variation of $\varrho G_{ij}$ with composition for water + acetone and for water + acetonitrile [12]. For other details see caption to Fig. 2.

Table 2 shows the values of the molar volumes and the isothermal compressibilities of the pure components used in Eqs. (26) and (27). The parameters $\alpha$ and $\beta$ are obtained by minimizing the following objective function

$$O.F. = \Sigma |G_{11}/G_{11,\text{ex}} - 1| + |G_{12}/G_{12,\text{ex}} - 1| + |G_{22}/G_{22,\text{ex}} - 1|$$  (30)
Fig. 9. The variation of $\varrho G_{ij}$ with composition for water + 2-aminoethanol [12] and for water + dimethylsulfoxide [12] (DMSO). For other details see caption to Fig. 2.

where $G_{ij,\text{ex}}$ is the experimental $G_{ij}$ and the summation runs over all the experimental points. Figs. 2—11 show the comparison between the experimental and predicted $G_{ij}$ values. The agreement ranges from excellent as in the case of TCM + dioxane, to poor as in the case of water + acetone and water + dioxane. The largest deviations are seen at the extrema. The experimental uncertainties are highest at these locations.
Fig. 10. The variation of $qG_{ij}$ with composition for water + methanol at two temperatures. For other details see caption to Fig. 2.

Table 3 shows the values of the parameters $\alpha$ and $\beta$. For the systems water + alcohol, both $\alpha$ and $\beta$ decrease with increasing the chain length, at the same temperature. The opposite behavior is seen for the $\alpha$ of the TCM + alcohol systems. The $G_{ij}$ integrals at different temperatures are obtained for the systems methanol + water and ethanol + water. The model gives better representation at higher temperatures. The parameter $\alpha$
and $\beta$ show monotonic variation with temperature for water + methanol, but not for water + ethanol.

Other systems will soon be considered to test the applicability of the model, in addition to searching for correlations between $\alpha$ and $\beta$ and molecular structure of the components.
Acknowledgement

This research is supported in part by the NATO Scientific Affairs Division and in part by the Chemical Sciences Division of the Office of Basic Energy Sciences, the U.S. Department of Energy Grant No. DE-FG02-84ER13229.

References

2. L. Boltzmann, Wiener Ber. 76 (1877) 373.