

Kirkwood–Buff Integrals in Aqueous Alcohol Systems: Comparison between Thermodynamic Calculations and X-Ray Scattering Experiments

I. Shulgin[†] and E. Ruckenstein*

Department of Chemical Engineering, State University of New York at Buffalo, Amherst, New York 14260

Received: August 18, 1998; In Final Form: January 19, 1999

Thermodynamic data were used to calculate the Kirkwood–Buff integrals for the aqueous solutions of methanol, ethanol, propanols, and butanols. The calculated values have been compared to those obtained from small-angle X-ray scattering (SAXS) experiments, and satisfactory agreement was found. Improved expressions have been suggested and used to calculate the excess number of molecules around central ones. On this basis, information about the structure of the solutions was gathered, the main conclusion being that the interactions among similar molecules prevail; this leads to clustering dominated by the same kind of molecules.

Introduction

Many models are available for describing the thermodynamic behavior of solutions.^{1–2} However, so far no one could satisfactorily simulate the solution behavior over the whole concentration range and provide the correct pressure and temperature dependencies. This generated interest in the thermodynamically rigorous theories of Kirkwood–Buff³ and McMillan–Mayer.⁴ In the present paper, the emphasis is on the application of the Kirkwood–Buff theory to the aqueous solutions of alcohols, because it is the only one which can describe the thermodynamic properties of a solution over the entire concentration range.⁵ The key quantities in the Kirkwood–Buff theory of solution are the so-called Kirkwood–Buff integrals (KBIs) defined as

$$G_{ij} = \int_0^\infty (g_{ij} - 1) 4\pi r^2 dr \quad i, j = 1, 2 \quad (1)$$

where g_{ij} is the radial distribution function between species i and j and r is the distance between the centers of molecules i and j . From the KBI's valuable information regarding the structural and energetic features of the binary, ternary and multicomponent solutions could be obtained.³ Ben-Naim indicated how to calculate the KBIs from measured thermodynamic properties.⁶ Since then, the KBIs have been calculated for numerous systems^{7–14} and the results used to examine the solution behavior with regard to (1) local composition, (2) various models for phase equilibrium, and (3) preferential solvation and others.^{15–18}

The KBIs could also be determined experimentally from small-angle X-ray scattering, small-angle neutron scattering (SANS) and light-scattering^{5,19–20} experiments. It is worth mentioning that SAXS and SANS experiments allow one to obtain not only the KBIs, but also to gather information about the formation of complexes and clusters in solutions.

Numerous SAXS determinations for aqueous alcohol solutions are available.^{20–30} The aqueous solutions of tertiary butanol (*tert*-butyl alcohol) were examined in refs 20–24, the methanol–water system in ref 25, and the aqueous solutions of ethanol in ref 26. The aqueous solutions of 1-propanol were studied in a number of papers,^{27–29} and the 2-propanol + water system was also investigated.^{27–28} It is worth mentioning that these inves-

tigations were performed over a wide range of concentrations and that measurements at different temperatures were conducted.^{24,28} All the systems investigated in refs 19–29 were homogeneous. SAXS measurements were also carried out for binary aqueous solutions of 1-butanol, 2-butanol, and iso-butanol for a few compositions near the transition to the two-phase region.³⁰ The aggregation or cluster formation was the subject of SAXS research as well: aggregates were identified in the aqueous systems of any of the propanols or butanols and the dependence of the aggregate size on composition obtained. SANS was much rarely employed; it was used to study the aqueous alcohol solutions at a few concentrations.¹⁹

The aqueous alcohol systems were chosen for the current research because (1) aggregation in these systems was found by several independent experimental methods; (2) while there are several investigations regarding their KBI's, there is no agreement between the reported data. This becomes clear if we compare the peak G_{11} values in the system 1-propanol (1)–water (2). (Throughout this paper, component 1 represents the alcohol and component 2 the water.) (3) For all the selected systems, accurate thermodynamic data are available. (4) Last but not least, SAXS data are available for most of the systems chosen (except the methanol–water system), but a systematic comparison between the KBI's extracted from the SAXS data and those obtained thermodynamically was not yet made.

Therefore the aim of this paper is to calculate the KBIs for aqueous solutions of alcohols from thermodynamic data, to compare the results to those obtained from SAXS measurements, and to examine some specific features regarding the structure of aqueous alcohol solutions.

Theory and Formulas. 1. *KBI's Calculation.* The main formulas for calculations^{7,13–14} are

$$G_{12} = G_{21} = RTk_T - \frac{V_1 V_2}{VD} \quad (2)$$

$$G_{ii} = G_{12} + \frac{1}{x_i} \left(\frac{V_i}{D} - V \right) \quad i \neq j \quad (3)$$

where

$$D = \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{P,T} x_i + 1 \quad (4)$$

In eqs 2–4, k_T is the isothermal compressibility, V_i is the partial

* To whom the correspondence should be addressed. E-mail: fealiru@acsu.buffalo.edu. Fax: (716) 645-3822.

[†] Current e-mail address: ishulgin@eng.buffalo.edu.

molar volume of component i , x_i is the molar fraction of component i , V is the molar volume of the mixture, T is the absolute temperature and γ_i is the activity coefficient of component i . Because the dependence of k_T on composition is not known for all the systems investigated and because of the small contribution of $RT k_T$ to the KBI's,⁷ the dependence of k_T on composition will be approximated by

$$k_T = k_{T,1}^0 \varphi_1 + k_{T,2}^0 \varphi_2 \quad (5)$$

where φ_i is the volume fraction of component i in solution and $k_{T,i}^0$ is the isothermal compressibility of the pure component i .

The analysis of the possible errors in the calculation of KBI's clearly indicated that the main error is introduced through the D value.^{7,31} The usual way for calculating D is from isothermal vapor–liquid equilibrium data, by assuming that

$$(\partial \ln \gamma_i / \partial x_i)_{P,T} = (\partial \ln \gamma_i / \partial x_i)_T \quad (6)$$

The main uncertainty in the derivative of the activity coefficient or partial pressure is caused by the vapor composition which is needed to calculate the activity coefficient or the partial pressure. Almost 35 years ago, Van Ness³² suggested to measure the dependence of the total pressure on liquid composition at constant temperature and to use the data to calculate the vapor composition and the activity coefficient. This suggestion has the advantage that the vapor pressure can be measured much more precisely than the vapor composition. As shown in Appendix 1, D can be related to the pressure via the expression

$$D = \frac{\left(\frac{\partial \ln P}{\partial x_1} \right)_T}{P_1^0 \gamma_1 - P_2^0 \gamma_2} \quad (7)$$

where P_1^0 and P_2^0 are the saturated vapor pressures of the pure components 1 and 2 at a given temperature T , and γ_i can be taken from experiment or calculated through any of the usual models, such as the Wilson, NRTL, or UNIQUAC model.²

At infinite dilution, the following limiting expressions are valid for KBIs^{7,13–14}

$$\lim_{x_i \rightarrow 0} G_{12} = RTk_{T,j}^0 - V_i^\infty \quad (8)$$

$$\lim_{x_i \rightarrow 1} G_{12} = RTk_{T,i}^0 - V_j^\infty \quad (9)$$

$$\lim_{x_i \rightarrow 0} G_{ii} = RTk_{T,j}^0 + V_j^0 - 2V_i^\infty - V_j^0 \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{P,T,x_i=0} \quad (10)$$

and

$$\lim_{x_i \rightarrow 1} G_{ii} = RTk_{T,i}^0 - V_i^0 \quad (11)$$

where V_i^0 is the molar volume of the pure component i and V_i^∞ is the partial molar volume of component i at infinite dilution. The limiting value $(\partial \ln \gamma_i / \partial x_i)_{P,T,x_i=0}$ was calculated using for the dilute region the following expression:³³

$$\left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{P,T} = k_i(P,T) \quad (12)$$

where $k_i(P,T)$ can be obtained directly from isothermal vapor–liquid equilibrium data in the dilute region.

2. *Excess Number of Molecules around a Central Molecule.* Almost all the considerations regarding the KBI's are based on the quantity

$$\Delta n_{ij} = c_i G_{ij} \quad (13)$$

(where c_i is the molar concentration of species i in the mixture) which is usually interpreted as the excess (or deficit) number of molecules i around a central molecule j .⁶

Matteoli and Lepori^{13,14} noted that Δn_{ij} calculated with eq 13 have nonzero values for ideal systems, even though they are expected to vanish. In addition, there are many systems for which all KBIs (G_{11} , G_{12} , and G_{22}) are negative in certain ranges of composition.^{17,34} As a result, in such cases all Δn_{ij} would be negative, and this is not possible.

Because the KBIs have nonzero instead of zero values for ideal systems, Matteoli and Lepori suggested to replace G_{ij} in eq 13 by $(G_{ij} - G_{ij}^{\text{id}})$ ^{13,14}

$$\Delta n_{ij}' = c_i (G_{ij} - G_{ij}^{\text{id}}) = c_i \Delta G_{ij} \quad (14)$$

with the KBIs for ideal systems (G_{ij}^{id}) given by the expressions^{13,14}

$$G_{12}^{\text{id}} = RTk_T^{\text{id}} - \frac{V_1^0 V_2^0}{V^{\text{id}}} = RTk_{T,2}^0 - V_1^0 - \varphi_1 (V_2^0 - V_1^0 + RTk_{T,2}^0 - RTk_{T,1}^0) \quad (15)$$

$$G_{11}^{\text{id}} = G_{12}^{\text{id}} + V_2^0 - V_1^0 \quad (16)$$

and

$$G_{22}^{\text{id}} = G_{12}^{\text{id}} - (V_2^0 - V_1^0) \quad (17)$$

where k_T^{id} and V^{id} are the isothermal compressibility and the molar volume of an ideal solution, respectively.

However, because “the volume occupied by the excess j molecules around an i molecule must be equal to the volume left free by the i molecules around the same i molecule”,¹³

$$V_j \Delta n_{ji}' = -V_i \Delta n_{ii}' \quad (18)$$

Equation 14 does not satisfy identically eq 18, because its insertion in the latter equation leads to

$$RTV(k_T - k_T^{\text{id}}) = V_i V + V_i (V_j^0 - V^{\text{id}}) - \frac{V_i^0 V_j^0 V}{V^{\text{id}}} \quad (19)$$

Equation 19 indicates that only if G_{ij}^{id} is replaced by G_{ij}^{v} (eqs 20 and 21), which is obtained from the former by substituting k_T^{id} , V_i^0 , and V^{id} with k_T , V_i , and V , respectively, can eq 18 be satisfied identically.

$$G_{12}^{\text{v}} = G_{21}^{\text{v}} = RTk_T - \frac{V_1 V_2}{V} \quad (20)$$

$$G_{ii}^{\text{v}} = G_{12}^{\text{v}} + V_j - V_i \quad i \neq j \quad (21)$$

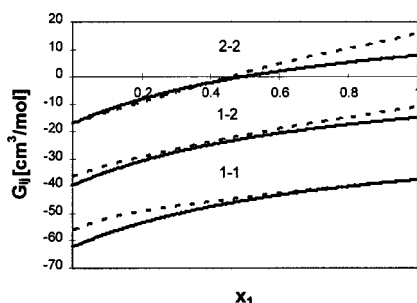


Figure 1. Comparison between G_{ij}^{id} and G_{ij}^{V} for methanol–water at 298.15 K. G_{ij}^{id} is given by the solid line and G_{ij}^{V} by the broken line.

TABLE 1: Peak G_{11} for the 1-Propanol–Water System

x_1 (max)	G_{11} [cm^3/mol]	ref
~ 0.25	~ 390	7
0.06	876	11
~ 0.15	~ 1900	12

TABLE 2: Original Data Used for Calculating the Kirkwood–Buff Integrals

system	D		V, V_1, V_2	
	data	ref	data	ref
methanol–water	$P-x-y, T = 298.14 \text{ K}$	35	$V^E, T = 298.15 \text{ K}$	36
ethanol–water	$P-x, T = 298.15 \text{ K}$	37	$V^E, T = 298.15 \text{ K}$	36
1-propanol–water	$P-x-y, T = 303.15 \text{ K}$	38	$V^E, T = 298.15 \text{ K}$	39
2-propanol–water	$P-x-y, T = 298.15 \text{ K}$	40	$V^E, T = 298.15 \text{ K}$	41
1-butanol–water	$P-x, T = 323.23 \text{ K}$	42	$V^E, T = 308.15 \text{ K}$	43
2-butanol–water	$P-x, T = 323.18 \text{ K}$	42	$V^E, T = 293.15 \text{ K}$	44
iso-butanol–water	$P-x, T = 323.15 \text{ K}$	42	$V^E, T = 293.15 \text{ K}$	45
tert-butanol–water	$P-x, T = 323.13 \text{ K}$	42	$V^E, T = 303.15 \text{ K}$	46

^a V^E is the excess volume.

Consequently

$$\Delta n_{12}' = c_1(G_{12} - G_{12}^{\text{V}}) = c_1\Delta G_{12} = c_1\Delta G_{21} = -\frac{c_1V_1V_2(1-D)}{V} \quad (22)$$

$$\Delta n_{21}' = c_2(G_{12} - G_{12}^{\text{V}}) = c_2\Delta G_{12} = c_2\Delta G_{21} = -\frac{c_2V_1V_2(1-D)}{V} \quad (23)$$

and

$$\Delta n_{ii}' = c_i\Delta G_{ii} = c_i(G_{ii} - G_{ii}^{\text{V}}) = \frac{c_i x_j V_j^2 (1-D)}{x_i V} \quad i \neq j \quad (24)$$

A comparison between G_{ij}^{V} and G_{ij}^{id} for the methanol–water system is presented in Figure 1. It is worth mentioning that for ideal mixtures $\Delta n_{ij}' = 0$.

Data Sources and Treatment Procedure. The calculation of the KBIs from thermodynamic data requires information about the dependence on composition of the following variables: D , molar volume V , partial molar volumes V_1 and V_2 , and the isothermal compressibility k_T . The sources of these data are listed in Table 2.

The vapor–liquid equilibrium data used in the calculations have been selected on the basis of the following two criteria: (1) the thermodynamic consistency tests (the integral test and the point test⁴⁷) should be fulfilled by the systems chosen, (2) the sets chosen should contain at least 10–15 experimental

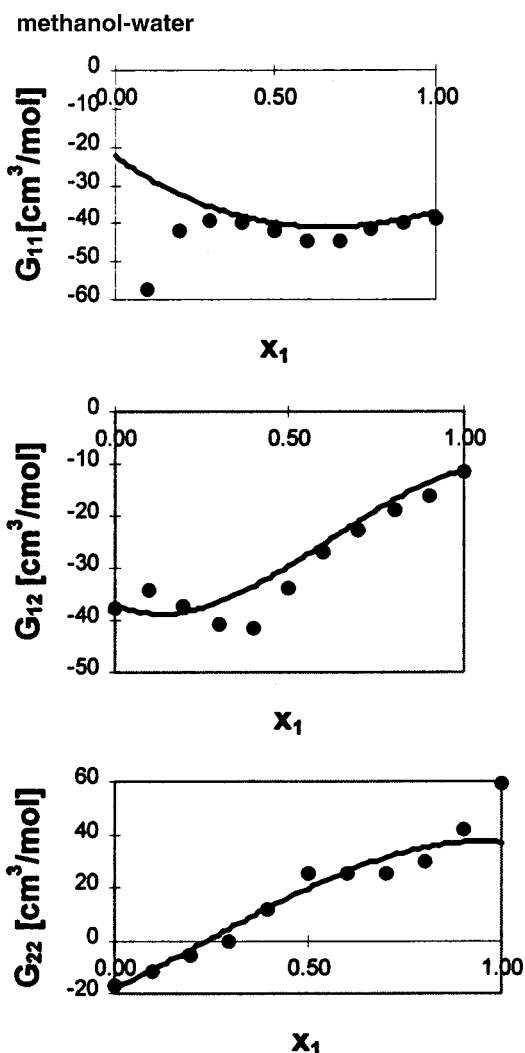


Figure 2. Comparison between G_{ij} calculated by us (solid lines) and ref 8 (●).

TABLE 3: The Sources for the Kirkwood–Buff Integrals from SAXS Measurements

system	data	ref
ethanol–water	$G_{ij}, T = 298.15 \text{ K}$	26
1-propanol–water	$G_{ij}, T = 293.15 \text{ K}$	27
	$G_{ij}, T = 298.15 \text{ K}$	29
2-propanol–water	$I(0), T = 293.15 \text{ K}$	27
1-butanol–water	$G_{ij}, T = 298.15 \text{ K}$	30
2-butanol–water	$G_{ij}, T = 298.15 \text{ K}$	30
iso-butanol–water	$G_{ij}, T = 298.15 \text{ K}$	30
tert-butanol–water	$G_{ij}, T = 293.15 \text{ K}$	23

points. For several systems the vapor–liquid equilibrium data and those for excess volume are available at different temperatures. This has no significant effect on the results.⁴⁸ The partial molar volumes at infinite dilution used for calculating the limiting values of KBIs have been taken from refs 49–52 or calculated from excess volume data.

The isothermal compressibilities have been calculated with eq 5, using for the isothermal compressibilities of the pure substances the data from refs 53–56 (only the value for 2-butanol was taken as that for isobutanol). The V^E data have been fitted using the Redlich–Kister equation.⁵⁷ The values of D have been obtained from the activity coefficients or total pressure data by the sliding polynomials method.⁵⁸ To check the accuracy of our calculations, the D values have been

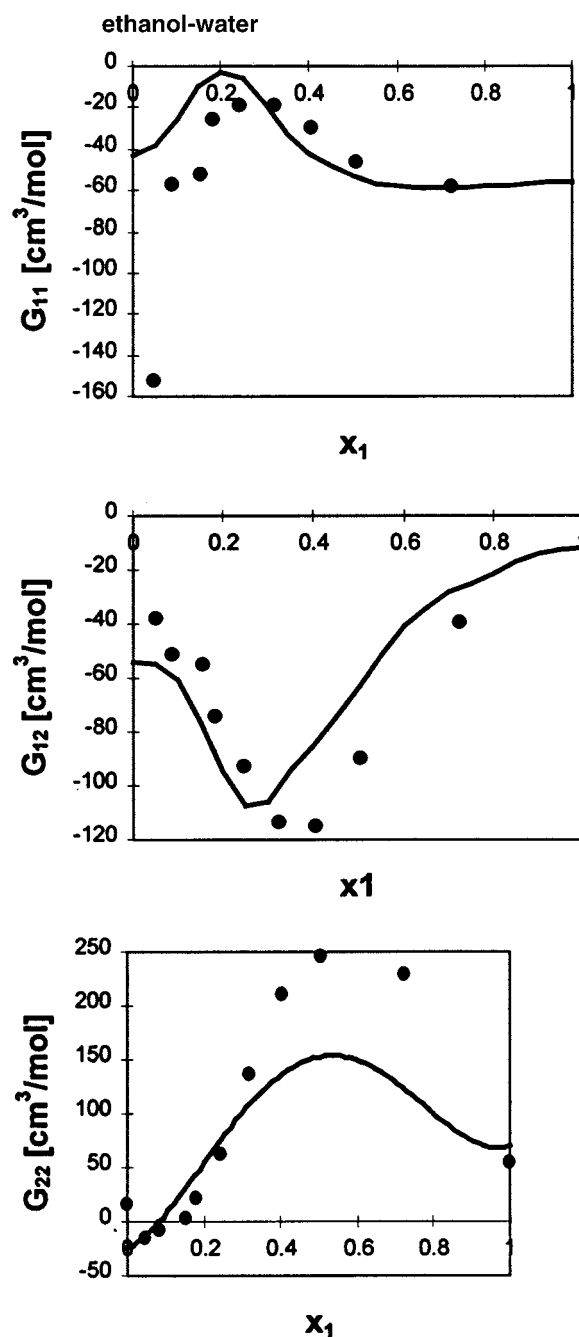


Figure 3. Comparison between the KBIs from thermodynamic calculations (solid line) and those from SAXS (●, ref 26).

additionally evaluated using the NRTL equation. The KBIs obtained from SAXS measurements were taken from the original publications,^{24–30} and the sources of the data are listed in Table 3.

The KBI's data for the 2-propanol–water system have been obtained from the so-called X-ray zero-angle intensity $I(0)$.²⁷ The equations used to calculate the KBIs are summarized in Appendix 2.

Results

A comparison between the KBIs obtained thermodynamically and those obtained from SAXS measurements is made in Figures 2–9. For the methanol–water system no SAXS data are

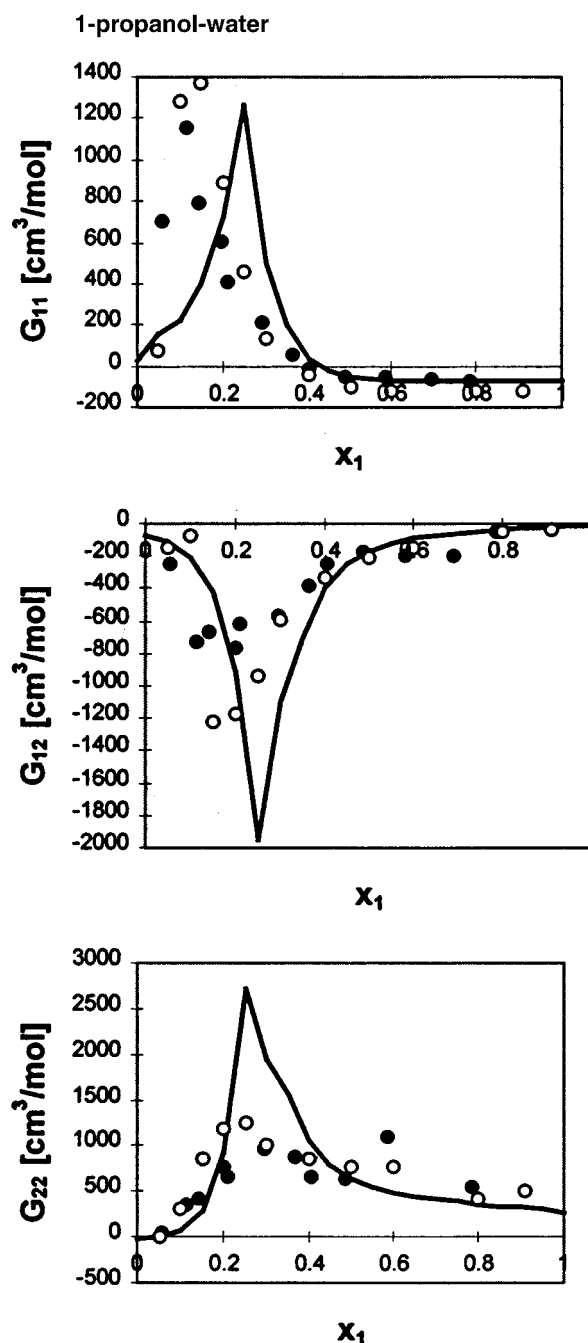


Figure 4. Comparison between the KBIs from thermodynamic calculations (solid line) and those from SAXS (●, ref 29; ○, ref 27).

available, and we compared our calculations to those of Donkersloot⁸ and found satisfactory agreement between the two sets (Figure 2). Only for G_{11} in the dilute range of methanol there are differences between the compared sets. However, by calculating the limiting values of KBIs with eqs 8–11 a value of G_{11}^0 equal to -25 ± 5 [cm³/mol] was found for $T = 298$ K, which is in good agreement with our results. Our calculations for the ethanol–water mixture (Figure 3) are in agreement with the G_{ij} obtained from the SAXS measurements,²⁶ with the exception of G_{11} at low concentrations of ethanol and the peak value of G_{22} . The limiting value of G_{11} (G_{11}^0), calculated using eq 10, and that obtained by extrapolating the results of the calculation for the nondilute region nearly coincide. The comparison of our results with those from SAXS measurements for 1- or 2-propanol–water systems (Figures 4 and 5) show agreement, except for the dilute region of the 2-propanol–water system.

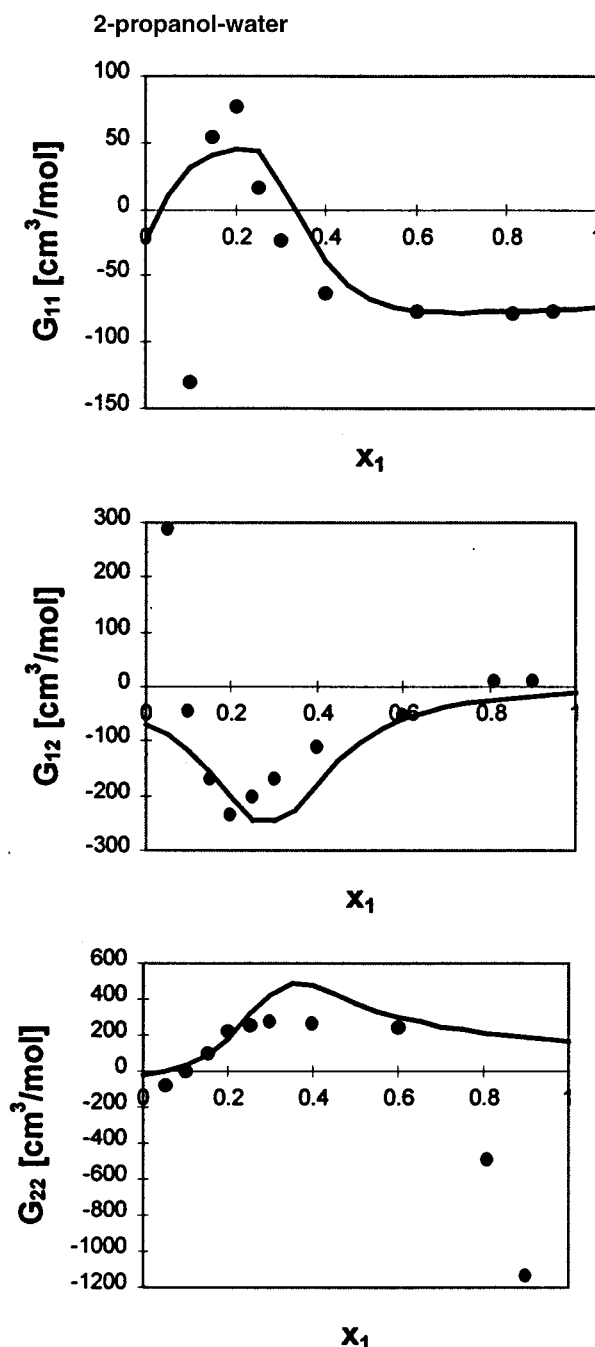


Figure 5. Comparison between the KBI's from thermodynamic calculations (solid line) and those from SAXS (●, ref 27).

The experiments provide somewhat lower values for G_{11} ($x_1 < 0.2$) and for G_{22} ($x_2 < 0.2$), but the limiting values G_{ij}^0 are in good agreement with the calculated extrapolated results. There are some differences in the peak values of the KBI's for the 1-propanol–water system. Table 1 shows that for this system there is a large scattering of the KBI's peaks. This scattering is caused by the difficulty to obtain reliable D values in the composition range $0 \leq x_1 \leq 0.3$. More precise vapor–liquid equilibrium data are needed to obtain more exact peak values for the KBI's. As well-known,^{42,51} the mixture *tert*-butyl alcohol–water (Figure 6) is in normal conditions the only homogeneous one among the butanol–water systems. The vapor–liquid equilibrium in this system was thoroughly investigated in ref 42, where it was also pointed out that it is difficult to describe the vapor–liquid equilibrium for this system with the conventional equations (e.g., NRTL and UNIQUAC equa-

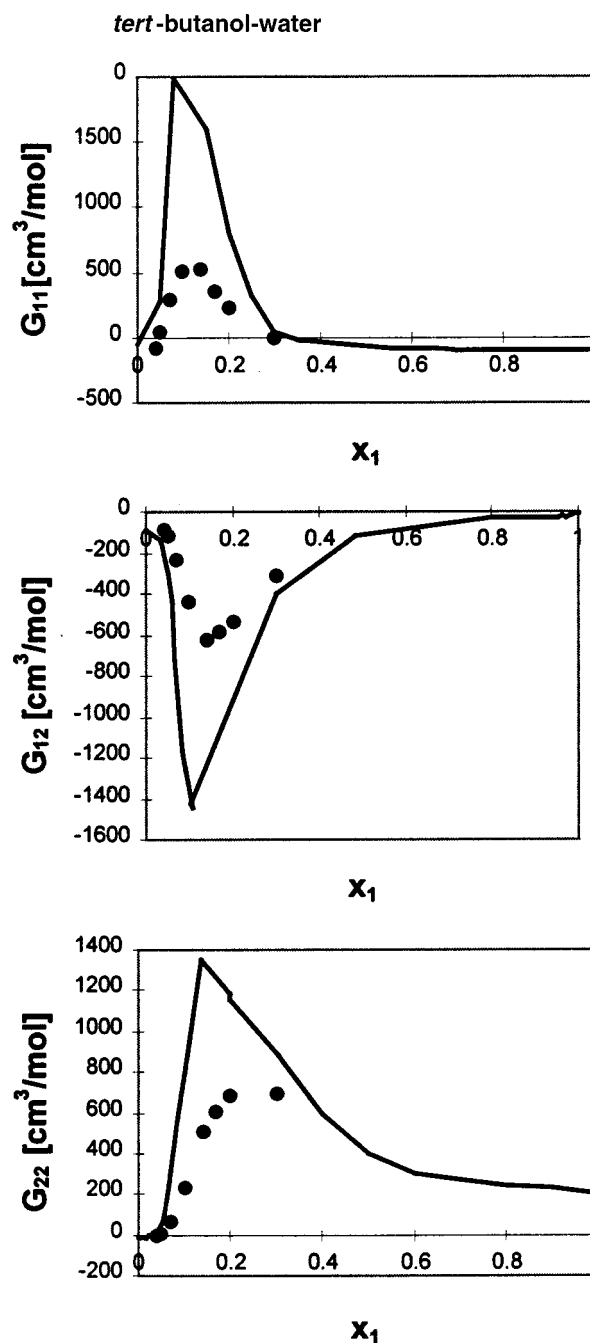


Figure 6. Comparison between the KBI's from thermodynamic calculations (solid line) and those from SAXS (●, ref 23).

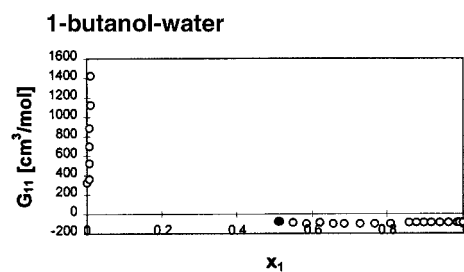


Figure 7. Comparison between the G_{11} from thermodynamic calculations (○, this work) and those from SAXS (●, ref 30).

tions wrongly indicate phase separation). This generates some deviations between the calculated KBI's and those obtained from SAXS measurements, in the composition range $0.06 \leq x_1 \leq 0.25$.

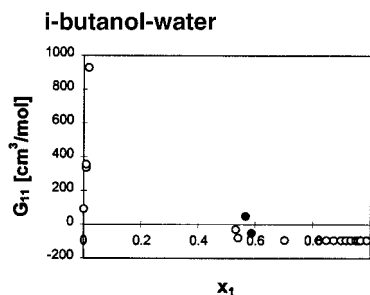


Figure 8. Comparison between the G_{11} from thermodynamic calculations (○, this work) and those from SAXS (●, ref 30).

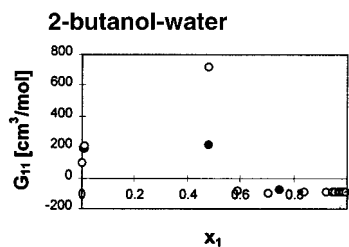


Figure 9. Comparison between the G_{11} from thermodynamic calculations (○, this work) and those from SAXS (●, ref 30).

Limited information is available concerning the KBI's for systems with phase separation. The KBI's for the 1-butanol–water system were calculated in ref 7. The behavior of the KBI's in all butanol (1-, 2-, and iso-)–water systems is similar (Figures 7–9). In these systems, the G_{ij} s change rapidly and become infinite at the phase separation point

$$\lim_{x_1 \rightarrow x_1^f} G_{ij} = \pm\infty \quad (25)$$

where x_1^f is the butanol concentration at the point where the mixture becomes partially miscible. In the butanol-rich region, G_{ij} tends to infinity when the concentration approaches the boundary of the two phase region. Only few SAXS data are available for the systems 1-, 2-, and iso-butanol + water,³⁰ and we found satisfactory agreement between the results of our calculations and the SAXS measurements.

Generally Figures 2–9 show satisfactory agreement between the KBI's calculated and those obtained from SAXS measurements.

Discussion

Using the expressions suggested in this paper, we calculated the excess number of molecules $\Delta n'_{ij}$ around a central one (eqs 22–24). Figure 10 provides the excess (or deficit) number of molecules in the vicinity of an alcohol molecule and Figure 11—in the vicinity of a water molecule as the central molecule.

The present calculations are in agreement with the conclusion of ref 59 (which employed both a lattice and the McMillan–Mayer theories of solution⁴) that the solute–solute interactions in the systems investigated increase in the sequence MeOH < EtOH < 2-PrOH < 1-PrOH \cong t-BuOH. There are, however, essential differences between the lower alcohols (MeOH and EtOH) and the higher ones.

Figures 10 and 11 reveal that, for the methanol–water and ethanol–water systems, the local compositions are close to the bulk ones over the entire concentration range. This means that,

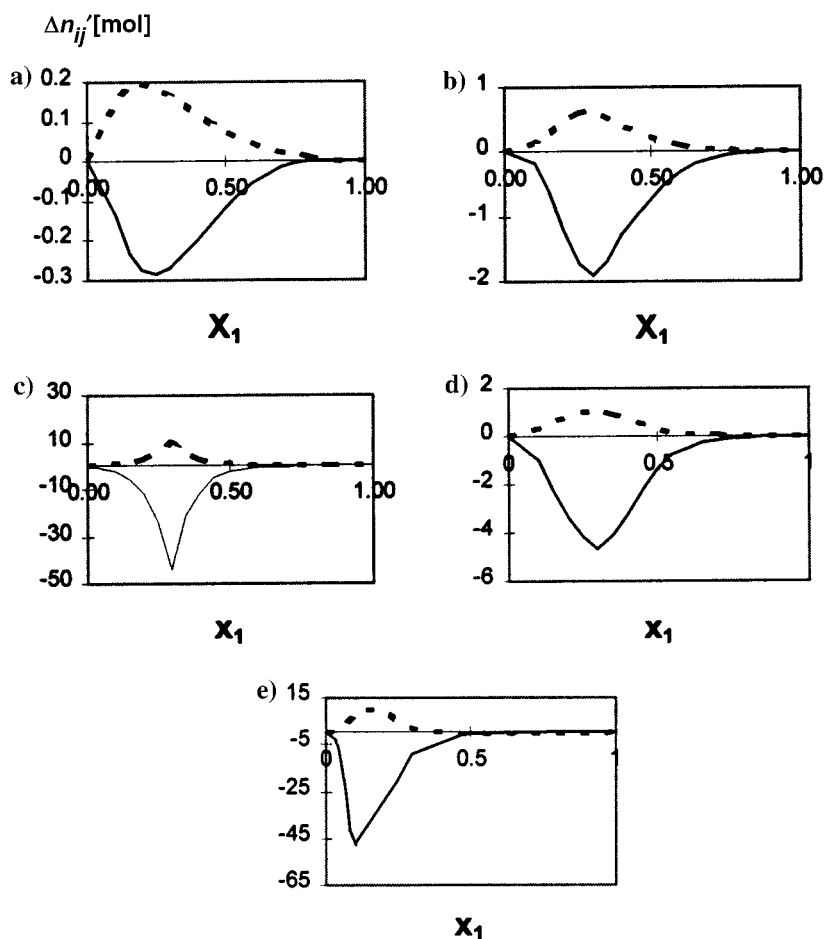


Figure 10. $\Delta n'_{ij}$ in the vicinity of an alcohol molecule. $\Delta n'_{11}$ is given by broken line, $\Delta n'_{21}$ by the solid line. (a) methanol–water, (b) ethanol–water, (c) 1-propanol–water, (d) 2-propanol–water, (e) *tert*-butanol–water.

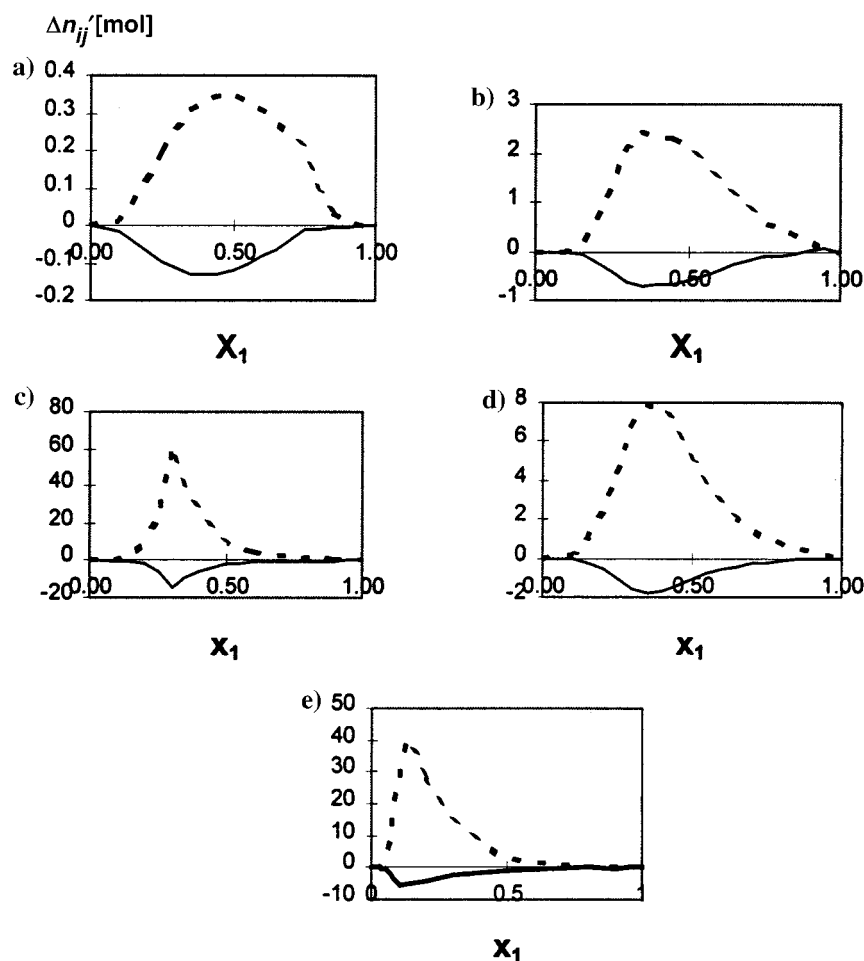


Figure 11. $\Delta n_{ij}'$ in the vicinity of a water molecule. $\Delta n_{22}'$ is given by the broken line, $\Delta n_{12}'$ by the solid line. (a) methanol–water, (b) ethanol–water, (c) 1-propanol–water, (d) 2-propanol–water, (e) *tert*-butanol–water.

in these systems, little clustering occurs, a conclusion in agreement with the SAXS measurements.^{25,26}

For the ethanol–water system, there are somewhat larger changes in the vicinity of a water molecule. Indeed, in the concentration range $0.25 < x_1 < 0.65$, $2.5 > \Delta n_{22}' > 1$ and small clusters, dominated by water molecules, seems to be generated. Figures 10 and 11 bring evidence for clustering in aqueous binary systems of 1- and 2-propanols and *tert*-butyl alcohol; SAXS experiments also indicated the presence of clusters in these systems.^{23–24,27–29}

One may note that the values of $\Delta n_{ij}'$ for the 2-propanol–water system are much smaller than those for 1-propanol–water and *tert*-butyl alcohol–water; they are, however, about twice as large as those in the ethanol–water system.

The calculation of the $\Delta n_{ij}'$ in aqueous systems of propanols and butanols indicates that clustering in these systems is caused by the accumulation of alcohol molecules near a central alcohol molecule and water molecule near a central molecules of water. This means that the hydrophobic interactions between the alcohol molecules and the interactions between water molecules are dominant in these systems.

Conclusion

The aqueous systems of methanol, ethanol, propanols, and butanols were examined in the framework of the Kirkwood–Buff theory of solution. The Kirkwood–Buff integrals were calculated using thermodynamic equations, in which the derivatives $(\partial \ln \gamma_i / \partial x_i)_{P,T}$ were expressed in terms of $(\partial \ln P / \partial x_i)_T$, which

can be more accurately determined from isothermal P – x data. The calculated KBI's were compared to those obtained from SAXS measurements and satisfactory agreement found.

New expressions for the excess number of molecules near a central molecule were suggested and used to calculate the distribution of species near the water or alcohol molecules as central ones. The main conclusion is that separate clusters of water and alcohol are formed and that the clustering increases with the length of the alcohol chain.

Acknowledgment. We are indebted to Dr. K. Fischer (University of Oldenburg, Germany) for providing information regarding the phase equilibria and excess volume.

Appendix 1

For vapor–liquid equilibrium in binary system with ideal behavior of the vapor phase one can write:^{1–2}

$$P = P_1^0 x_1 \gamma_1 + P_2^0 x_2 \gamma_2 \quad (\text{A1-1})$$

Differentiating with respect to x_1 for isothermal condition, one obtains

$$\left(\frac{\partial P}{\partial x_1} \right)_T = P_1^0 \gamma_1 - P_2^0 \gamma_2 + P_1^0 x_1 \left(\frac{\partial \gamma_1}{\partial x_1} \right)_T - P_2^0 x_2 \left(\frac{\partial \gamma_2}{\partial x_2} \right)_T \quad (\text{A1-2})$$

According to eq 4

$$x_1 \left(\frac{\partial \gamma_1}{\partial x_1} \right)_T = \gamma_1 (D - 1) \quad (\text{A1-3})$$

and

$$x_2 \left(\frac{\partial \gamma_2}{\partial x_2} \right)_T = \gamma_2 (D - 1) \quad (\text{A1-4})$$

Inserting the last two equations in eq A1-2 yields

$$D = \frac{\left(\frac{\partial P}{\partial x_1} \right)_T}{P_1^0 \gamma_1 - P_2^0 \gamma_2} \quad (\text{A1-5})$$

For nonideal vapor phase, corrections for nonideality should be included.^{1–2}

Appendix 2

To calculate the KBIs from the SAXS data for the 2-propanol–water mixture, the following equations were used:^{23,27,60}

$$\frac{I(0)}{\bar{N}} = \frac{\bar{N}}{v} k_B T z^2 k_T + [z\delta - (z_1 - z_2)]^2 [\bar{N} \langle (\Delta x_1)^2 \rangle] \quad (\text{A2-1})$$

$$\langle \Delta N \Delta x_1 \rangle = -\delta \bar{N} \langle (\Delta x_1)^2 \rangle \quad (\text{A2-2})$$

$$\langle (\Delta N)^2 \rangle / \bar{N} = \frac{\bar{N}}{v} k_B T k_T + \delta^2 \bar{N} \langle (\Delta x_1)^2 \rangle \quad (\text{A2-3})$$

where \bar{N} is the mean total number of molecules in the considered volume v of mixture, z_1 , z_2 , and z are average numbers of electrons per mole of alcohol, water, and mixture, respectively, k_B is the Boltzman constant, $\delta = (\bar{N}/v)(V_1 - V_2)$ is the dilatation factor, $\bar{N} \langle (\Delta x_1)^2 \rangle$, $\langle (\Delta N)^2 \rangle / \bar{N}$, and $\langle \Delta x_1 \Delta N \rangle$ are the mean-square fluctuation in concentration, the mean-square fluctuation in particle number, and their correlation, respectively.

The three kinds of fluctuations have been obtained from eqs A2-1–A2-3, and the KBIs have been calculated using the expressions:

$$G_{11} = \frac{v}{\bar{N}} \left\{ \frac{1}{x_1^2} [x_1^2 \langle (\Delta N)^2 \rangle / \bar{N} + 2x_1 \langle \Delta N \Delta x_1 \rangle + \bar{N} \langle (\Delta x_1)^2 \rangle - x_1 x_2] - 1 \right\} \quad (\text{A2-4})$$

$$G_{22} = \frac{v}{\bar{N}} \left\{ \frac{1}{x_2^2} [x_2^2 \langle (\Delta N)^2 \rangle / \bar{N} - 2x_2 \langle \Delta N \Delta x_1 \rangle + \bar{N} \langle (\Delta x_1)^2 \rangle - x_1 x_2] - 1 \right\} \quad (\text{A2-5})$$

$$G_{12} = \frac{v}{\bar{N}} \left\{ \frac{1}{x_1 x_2} [x_1 x_2 \langle (\Delta N)^2 \rangle / \bar{N} + (x_2 - x_1) \langle \Delta N \Delta x_1 \rangle - \bar{N} \langle (\Delta x_1)^2 \rangle] \right\} \quad (\text{A2-6})$$

References and Notes

- (1) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.
- (2) Prausnitz, J. M.; Lichtenhaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid–Phase Equilibria*, 2nd ed.; Prentice–Hall: Englewood Cliffs, NJ, 1986.
- (3) Kirkwood, J. G.; Buff, F. P. *J. Chem. Phys.* **1951**, *19*, 774.
- (4) McMillan, W.; Mayer, J. J. *J. Chem. Phys.* **1945**, *13*, 276.
- (5) Kato, T.; Fujiyama, T.; Nomura, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3368.
- (6) Ben-Naim, A. *J. Chem. Phys.* **1977**, *67*, 4884.
- (7) Matteoli, E.; Lepori, L. *J. Chem. Phys.* **1984**, *80*, 2856.
- (8) Donkersloot, M. C. A. *J. Solution Chem.* **1979**, *8*, 293.
- (9) Patil, K. J. *J. Solution Chem.* **1981**, *10*, 315.
- (10) Zaitsev, A. L.; Kessler, Y. M.; Petrenko, V. E. *Zh. Fiz. Khim.* **1985**, *59*, 2728.
- (11) Cheng, Y.; Page, M.; Jolicœur, C. *J. Phys. Chem.* **1993**, *93*, 7359.
- (12) Patil, K. J.; Mehra, G. P.; Dhondge, S. S. *Indian J. Chem.* **1994**, *33A*, 1069.
- (13) Matteoli, E.; Lepori, L. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 431.
- (14) Matteoli, E. *J. Phys. Chem. B* **1997**, *101*, 9800.
- (15) Ben-Naim, A. *Pure Appl. Chem.* **1990**, *62*, 25.
- (16) Pfund, D. M.; Lee, L. L.; Cochran, H. D. *Fluid Phase Equil.* **1988**, *39*, 161.
- (17) Rubio, R. G.; et al. *J. Phys. Chem.* **1987**, *91*, 1177.
- (18) Ben-Naim, A. *Cell Biophys.* **1988**, *12*, 3694.
- (19) D'Arrigo, G.; Teixeira, J. J. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1503.
- (20) Bale, H. D.; Sherplur, R. E.; Sorgen, D. K. *Phys. Chem. Liq.* **1968**, *1*, 181.
- (21) Koga, Y. *Chem. Phys. Lett.* **1984**, *111*, 176.
- (22) Nishikawa, K. *Chem. Phys. Lett.* **1986**, *132*, 50.
- (23) Nishikawa, K.; Kadera, Y.; Iijima, T. *J. Phys. Chem.* **1987**, *91*, 3694.
- (24) Nishikawa, K.; Hayashi, H.; Iijima, T. *J. Phys. Chem.* **1989**, *93*, 6559.
- (25) Donkersloot, M. C. A. *Chem. Phys. Lett.* **1979**, *60*, 435.
- (26) Nishikawa, K.; Iijima, T. *J. Phys. Chem.* **1993**, *97*, 10824.
- (27) Hayashi, H.; Nishikawa, K.; Iijima, T. *J. Phys. Chem.* **1990**, *94*, 8334.
- (28) Hayashi, H.; Udagawa, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 155.
- (29) Shulgin, I.; Serimaa, R.; Torkkeli, M. Report Series in Physics HU-P-256; Helsinki, 1991.
- (30) Shulgin, I.; Serimaa, R.; Torkkeli, M. Helsinki, 1991. Unpublished Data.
- (31) Zaitsev, A. L.; Petrenko, V. E.; Kessler, Y. M. *J. Solution Chem.* **1989**, *18*, 115.
- (32) Van Ness, H. *Classical Thermodynamics of Non-Electrolyte Solution*; Pergamon Press: New York, 1964.
- (33) Debenedetti, P. G.; Kumar, S. K. *AIChE J.* **1986**, *32*, 1253.
- (34) Marcus, Y. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 427.
- (35) Kooner, Z. S.; Phutela, R. C.; Fenby, D. V. *Aust. J. Chem.* **1980**, *33*, 9.
- (36) Benson, G. C.; Kiyohara, O. *J. Solution Chem.* **1980**, *9*, 791.
- (37) Rarey, J. R.; Gmehling, J. *Fluid Phase Equil.* **1993**, *65*, 308.
- (38) Udovenko, V. V.; Mazanko, T. F. *Izv. Vyssh. Uchebn. Zaved. Khim. Tekhnol.* **1972**, *15*, 1654.
- (39) Dethlefsen, C.; Sorensen, P. G.; Hvidt, A. *J. Solution Chem.* **1984**, *13*, 191.
- (40) Sazonov, V. P. *Zh. Prikl. Khim.* **1986**, *59*, 1451.
- (41) Davis, M. I.; Ham, E. S. *Thermochim. Acta* **1991**, *190*, 251.
- (42) Fischer, K.; Gmehling, J. *J. Chem. Eng. Data* **1994**, *39*, 309.
- (43) Singh, P. P.; Sharma, P. K.; Maken, S. *Indian J. Technol.* **1993**, *31*, 17.
- (44) Altsybeeva, A. L.; Belousov, V. P.; Ovtrakt, N. V. *Zh. Fiz. Khim.* **1964**, *38*, 1243.
- (45) Nakanishi, K. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 793.
- (46) Kim, E. S.; Marsh, K. N. *J. Chem. Eng. Data* **1988**, *33*, 288.
- (47) Gmehling, J.; et al. *Vapor–Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series I; DECHEMA: Frankfurt, 1977–1996 (in 19 parts).
- (48) Zielkiewicz, J. *J. Phys. Chem.* **1995**, *99*, 3357.
- (49) Friedman, M. E.; Scheraga, H. A. *J. Phys. Chem.* **1965**, *69*, 3795.
- (50) Franks, F.; Smith, H. T. *J. Chem. Eng. Data* **1968**, *13*, 538.
- (51) Franks, F.; Desnoyers, J. E. *Water Sci. Rev.* **1985**, *1*, 171.
- (52) Sakurai, M.; Nakagawa, T. *J. Chem. Thermodyn.* **1984**, *16*, 171.
- (53) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 77th ed.; CRC Press: Boca Raton, 1996–1997.
- (54) Hellwege, K.-H., Ed. *Landolt–Boernstein: Numerical Data and Functional Relationship in Science and Technology: New Series*; Springer-Verlag: Berlin, 1979.
- (55) Diaz Pena, M.; Tardajos, G. *J. Chem. Thermodyn.* **1979**, *11*, 441.
- (56) Moriyoshi, T.; Inubushi, H. *J. Chem. Thermodyn.* **1977**, *9*, 587.
- (57) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.
- (58) Savitsky, A.; Gulay, M. J. F. *Anal. Chem.* **1964**, *36*, 1627.
- (59) Kozak, J. J.; Knight, W. S.; Kauzmann, W. *J. Chem. Phys.* **1968**, *48*, 675.
- (60) Bhatia, A. B.; Thornton, D. E. *Phys. Rev. B* **1970**, *2*, 3004.