

# Kirkwood–Buff Integrals in Aqueous Alcohol Systems: Aggregation, Correlation Volume, and Local Composition

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Received: September 11, 1998; In Final Form: December 2, 1998

The Kirkwood–Buff theory of solution was used to investigate the formation of clusters in aqueous alcohol solutions. The correlation volume (volume in which the composition differs from the bulk one) was calculated for the systems 1-propanol–water and *tert*-butyl alcohol–water and compared with the sizes of clusters determined by various physical techniques. The calculations indicated that two types of clusters, alcohol- and water-rich clusters, are present in the solutions. Their sizes, which depend on composition in a similar way, exhibit maxima in the water-rich region. The calculated values are in a satisfactory agreement with experiment. The composition inside the clusters (the local composition) was calculated as a function of the correlation volume for dilute aqueous methanol, ethanol, propanols, and *tert*-butyl alcohol solutions. The results were compared with the local compositions provided by the Wilson and NRTL equations.

## Introduction

The alcohol–water systems have attracted attention<sup>1–5</sup> for a number of reasons:

They are used as industrial solvents for small- and large-scale separation processes,<sup>2</sup> and they have unusual thermodynamic properties, which depend in a complicated manner on composition, pressure, and temperature; for example, the excess molar enthalpy ( $H^E$ ) of ethanol + water mixture against concentration exhibits three extrema in its dependence on composition at 333.15 K and 0.4 MPa.<sup>6</sup> The thermodynamic behavior of these systems is particularly intricate in the water-rich region, as illustrated by the dependencies of the molar heat capacity and partial molar volume on composition.<sup>7–9</sup> This sensitivity of the partial molar properties indicates that structural changes occur in the water-rich region of these mixtures.<sup>2,3</sup> Of course, the unique structural properties of water are responsible for this behavior.<sup>5,10</sup>

One of the peculiar features of the alcohol–water systems is the clustering that takes place in the solutions of the higher alcohol members (PrOH, BuOH, and higher). Direct experimental evidence regarding clustering was provided by small-angle X-ray scattering (SAXS),<sup>11–18</sup> small-angle neutron scattering (SANS),<sup>19</sup> light scattering (LS),<sup>20–23</sup> fluorescence emission spectroscopy,<sup>24</sup> microwave dielectric analysis,<sup>25</sup> and adsorption.<sup>26</sup> No clustering could be found, however, in the aqueous solutions of methanol and ethanol.<sup>27,28</sup> The results obtained by SAXS, SANS, and LS are summarized in Table 1.

The data in Table 1 show that clustering occurs in the water-rich region of solutions of propanols and *tert*-butyl alcohol, for alcohol molar fractions <0.3–0.4. Numerous models have been suggested to explain the properties of water–alcohol mixtures. They can be roughly subdivided in the following groups: (a) Chemical models<sup>5,29–33</sup>, based on chemical equilibrium between clusters and the constituent components, which can explain some thermodynamic properties of these solutions, but involve

oversimplified descriptions of the structure of the alcohol–water mixtures;<sup>2</sup> (b) clathrate-like models for dilute aqueous solutions of several alcohols;<sup>13,15,34</sup> (c) micellar-like models in which the alcohol molecules aggregate like surfactants in water, with the alkyl chain inside and the polar OH group outside;<sup>19</sup> (d) models that combine any of the above models with the representation of water as ice-like domains.<sup>29–30,35</sup> In the latter cases, the solution behavior in the water-rich region was attributed to a second-order phase transition involving the disordering of an ice-like network;<sup>36,37</sup> (e) the Kirkwood–Buff theory<sup>38</sup> provides a useful tool for the investigation of the structural features of solutions. The latter approach became popular particularly after Ben-Naim,<sup>39</sup> using the Kirkwood–Buff equations,<sup>38</sup> calculated the integrals  $G_{ij}$  (KBI)

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

from measurable macroscopic thermodynamic properties. In the relation of eq 1,  $g_{ij}$  is the radial distribution function between species  $i$  and  $j$  and  $r$  is the distance between the centers of molecules  $i$  and  $j$ . The KBIs have been calculated for numerous binary and ternary systems including the water–alcohol mixtures<sup>40–48</sup> and used to examine the solution behavior regarding the local composition, preferential solvation, and various models for phase equilibria.<sup>49–52</sup> In this paper, the KBI combined with the NRTL expression<sup>53,54</sup> for the local composition will be utilized for the calculation of the correlation volume (the volume in which the composition differs from the bulk composition). The correlation volumes for several alcohol–water systems will be calculated and compared with the sizes of clusters determined by various physical techniques (Table 1).

## Theory and Formulas

**1. Excess Number of Molecules near a Central One.** The key quantities in the Kirkwood–Buff approach are the integrals

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

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TABLE 1: Clustering in Aqueous Solutions of Alcohols

system	method	clustering	size (Å) <sup>a</sup>	composition range (x <sub>1</sub> )	temperature (K)	reference
MeOH/H <sub>2</sub> O	SAXS	no			298.15	27
EtOH/H <sub>2</sub> O	SAXS	no			293.15	28
1-PrOH/H <sub>2</sub> O	SAXS	yes	3–13.5	0.05–0.3	293.15	15
	SAXS	yes	—	—	278.15	16
	SAXS	yes	2–12	0.056–0.365	298.15	17
1-PrOH/D <sub>2</sub> O	LS	yes	8	0.05–0.4	298.15	20
	SANS	yes	14.4	0.114	298.15	19
	SANS	yes	18.7	0.114	278.15	19
2-PrOH/H <sub>2</sub> O	SAXS	yes	1.5–6.5	0.1–0.3	293.15	15
2-PrOH/D <sub>2</sub> O	SANS	yes	7.4	0.234	298.15	19
1-BuOH/H <sub>2</sub> O	SAXS	yes	8.2	0.018	298.15	18
2-BuOH/H <sub>2</sub> O	SAXS	yes	9	0.041	298.15	18
	SAXS	yes	12	0.48	298.15	18
<i>i</i> -BuOH/H <sub>2</sub> O	SAXS	yes	13	0.019	298.15	18
	SAXS	yes	13	0.568	298.15	18
<i>t</i> -BuOH/H <sub>2</sub> O	SAXS	yes	—	—	278.15	11
	SAXS	yes	—	—	300.15	11
	SAXS	yes	—	—	329.15	11
	SAXS	yes	0–17.1	0.05–0.4	300.15	12
	SAXS	yes	—	—	293.15	13
	SAXS	yes	3–19	0.05–0.3	293.15–348.15	14
	SANS	yes	29.1	0.107	278.15	19
<i>t</i> -BuOH/D <sub>2</sub> O	SANS	yes	18.4	0.107	298.15	19
	SANS	yes	30.4	0.107	310.15	19
	LS	yes	9.8–22	0.0725–0.26	257.15–345.15	21
	LS	yes	9.3–19	0.04–0.27	298.15–318.15	23

In Table 1,  $x_1$  is the molar fraction of alcohol (throughout this paper, component 1 represents alcohol and component 2, water). <sup>a</sup> The size is given by the Debye correlation length ( $l_D$ ), which is related to the radius of the cluster ( $R_C$ ) through the expression  $l_D = 1.1R_C$ .<sup>13,14</sup>

where  $c_i$  is the molar concentration of species  $i$  in the mixture and  $c_i G_{ij}$  represents the excess (or deficit) number of molecules  $i$  around a central molecule  $j$ .<sup>39</sup> The integrals  $G_{ij}$  (see *Appendix* for their expressions in terms of macroscopic thermodynamic quantities<sup>40</sup>) provide information about the tendency of molecules to stay away or to aggregate. However, these integrals have finite values for ideal solutions, which should be considered nonaggregated. Consequently, a better measure of the above tendency of the molecules can be obtained by introducing new quantities,  $\Delta n_{ij}$ , defined with respect to a reference state. Matteoli and Lepori<sup>46,47</sup> suggested to use the ideal mixture as the reference state and hence considered that the excess (or deficit) number of molecules  $i$  around a central molecule  $j$  is given by

$$\Delta n_{ij} = c_i(G_{ij} - G_{ij}^{id}) = c_i \Delta G_{ij} \quad (3)$$

where  $G_{ij}^{id}$  are the KBIs of an ideal system (See *Appendix* for their expressions in terms of macroscopic thermodynamic quantities<sup>40,46,47</sup>). However,  $\Delta n_{ij}$  are not independent quantities, because the volume occupied by the excess  $i$  molecules around an  $i$  molecule must be equal to the volume left free by the  $j$  molecules around the same  $i$  molecule.<sup>46</sup> This volume conservation condition leads to

$$V_j \Delta n_{ji} = -V_i \Delta n_{ii} \quad (4)$$

where  $V_i$  is the partial molar volume of component  $i$ . Eq 3 does not satisfy identically eq 4, because its insertion in the latter equation leads to

$$RTV(k_T - k_T^{id}) = V_i V + V_i(V_j^0 - V_j^{id}) - \frac{V_i^0 V_j^0 V}{V_j^{id}} \quad (5)$$

where  $k_T$  and  $V$  are the isothermal compressibility and the molar volume of the liquid mixture, respectively, the superscript “id” indicates ideal mixture, the superscript 0 refers to the pure

component,  $R$  is the universal gas constant, and  $T$  is the temperature in Kelvin. Eq 4 is satisfied identically only if  $k_T^{id}$ ,  $V_i^0$ , and  $V_j^{id}$  are replaced in the expressions of  $G_{ij}^{id}$  with  $k_T$ ,  $V_i$ , and  $V_j$ , respectively. Consequently,  $G_{ij}^{id}$  in eq 3 has to be replaced with  $G_{ij}^V$ , which is given by the following expressions<sup>48</sup>

$$G_{12}^V = G_{21}^V = RTk_T - \frac{V_1 V_2}{V} \quad (6)$$

$$G_{ii}^V = G_{12}^V + V_j - V_i \quad i \neq j \quad (7)$$

Consequently  $\Delta n_{ij}$  can be written as

$$\Delta n_{12} = c_1(G_{12} - G_{12}^V) = c_1 \Delta G_{12} = c_1 \Delta G_{21} = -\frac{c_1 V_1 V_2 (1 - D)}{V} \quad (8)$$

$$\Delta n_{21} = c_2(G_{12} - G_{12}^V) = c_2 \Delta G_{12} = c_2 \Delta G_{21} = -\frac{c_2 V_1 V_2 (1 - D)}{V} \quad (9)$$

and

$$\Delta n_{ii} = c_i \Delta G_{ii} = c_i(G_{ii} - G_{ii}^V) = \frac{c_i x_j V_j^2 (1 - D)}{x_i V} \quad i \neq j \quad (10)$$

where  $D$  is given by

$$D = \left( \frac{\partial \ln \gamma_i}{\partial x_i} \right)_{P,T} x_i + 1 \quad (11)$$

In eq 11,  $\gamma_i$  is the activity coefficient of component  $i$ ,  $P$  is the pressure, and  $x_i$  is the molar fraction of component  $i$  in the mixture. Eqs 8–10 have been used<sup>48</sup> to calculate the  $\Delta n_{ij}$  for the aqueous solutions of the following alcohols: MeOH, EtOH,

1-PrOH, 2-PrOH, and *t*-BuOH. It should be noted that for ideal mixtures  $\Delta n_{ij} = 0$ .

**2. Local Composition and Correlation Volume.** One of the most attractive features of the Kirkwood–Buff approach is its capability to provide values for the local composition.<sup>49,52</sup> Let us consider a molecule *i* whose correlation volume is  $V_{\text{cor}}^i$ . The total number of molecules *i* and *j* in this volume is given by the expressions

$$n_{ii} = \Delta n_{ii} + c_i V_{\text{cor}}^i \quad (12)$$

and

$$n_{ji} = \Delta n_{ji} + c_j V_{\text{cor}}^j \quad (13)$$

Consequently the local molar fractions,  $x_{ii}$  and  $x_{ji}$ , can be expressed as

$$x_{ii} = \frac{n_{ii}}{n_{ii} + n_{ji}} = \frac{\Delta n_{ii} + c_i V_{\text{cor}}^i}{\Delta n_{ii} + \Delta n_{ji} + (c_i + c_j) V_{\text{cor}}^i} \quad (14)$$

and

$$x_{ji} = \frac{n_{ji}}{n_{ii} + n_{ji}} = \frac{\Delta n_{ji} + c_j V_{\text{cor}}^j}{\Delta n_{ii} + \Delta n_{ji} + (c_i + c_j) V_{\text{cor}}^i} \quad (15)$$

Combining with eqs 8–10 and taking into account that  $c_j = n_j/V$  and  $x_j = n_j/\sum n_i$ , where  $n_j$  is the number of moles of component *j* in solution and  $V$  is the solution volume, eqs 14 and 15 become

$$x_{ii} = \frac{x_i(G_{ii} - G_{ii}^V) + x_i V_{\text{cor}}^i}{x_i(G_{ii} - G_{ii}^V) + x_j(G_{ji} - G_{ji}^V) + V_{\text{cor}}^i} \quad (16)$$

and

$$x_{ji} = \frac{x_j(G_{ji} - G_{ji}^V) + x_j V_{\text{cor}}^j}{x_i(G_{ii} - G_{ii}^V) + x_j(G_{ji} - G_{ji}^V) + V_{\text{cor}}^i} \quad (17)$$

Similar equations can be written for the local composition near a central molecule *j*. To calculate the correlation volumes with eqs 16 and 17, it is necessary to express  $x_{ii}$ ,  $x_{ji}$ ,  $G_{ij}$ ,  $G_{ij}^V$  as a function of composition. The values of  $G_{ij}$ ,  $G_{ij}^V$  for the systems investigated were calculated in our previous paper.<sup>48</sup> For  $x_{ii}$  and  $x_{ji}$ , the Wilson<sup>55</sup> and NRTL<sup>53</sup> equations can be used. Although not always satisfactory,<sup>56</sup> the NRTL expression represents the local composition better than the Wilson equation.<sup>56</sup> The NRTL provides the following expressions for the local compositions:<sup>53</sup>

$$x_{ii} = \frac{x_i}{x_i + x_j \exp(-\alpha_{12}\tau_{ji})} \quad (18)$$

$$x_{ji} = \frac{x_j \exp(-\alpha_{12}\tau_{ji})}{x_i + x_j \exp(-\alpha_{12}\tau_{ji})} \quad (19)$$

where  $\alpha_{12}$ ,  $\tau_{ji}$  are parameters. The Wilson model leads to the following expressions for the local compositions:<sup>55</sup>

$$x_{ii} = \frac{x_i}{x_i + x_j \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right)} \quad (20)$$

and

$$x_{ji} = \frac{x_j \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right)}{x_i + x_j \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right)} \quad (21)$$

where  $(\lambda_{ij} - \lambda_{ii})$  are parameters in the Wilson equation.

**3. Local Composition in the Dilute Region.** Let us consider the alcohol molecule as the central one (*i* = 1). Consequently, for the dilute region of alcohol one can write that

$$V_1 = V_1^\infty \quad (22)$$

$$V_2 = V_2^0 \quad (23)$$

$$V = x_1 V_1^\infty + x_2 V_2^0 \quad (24)$$

$$V_{\text{cor}}^1 = V_{\text{cor}}^1(P, T) \quad (25)$$

where  $V_i^0$  and  $V_i^\infty$  are the molar volume of the pure component *i* and the partial molar volume of component *i* at infinite dilution, respectively. In addition, in the dilute region<sup>57</sup>

$$D = K(P, T)x_1 + 1 \quad (26)$$

where<sup>57</sup>

$$K(P, T) = \left( \frac{\partial \ln \gamma_1}{\partial x_1} \right)_{P, T, x_1 \rightarrow 0}$$

Inserting expressions 22–26 into eq 16 yields

$$x_{11} = \frac{\alpha_1(P, T)x_1 + \alpha_2(P, T)x_1^2 + \alpha_3(P, T)x_1^3}{\beta_0(P, T) + \beta_1(P, T)x_1 + \beta_2(P, T)x_1^2} \quad (27)$$

and

$$x_{21} = 1 - x_{11} \quad (28)$$

where

$$\alpha_1 = -(V_2^0)^2 K + V_{\text{cor}}^1 V_2^0$$

$$\alpha_2 = (V_2^0)^2 K + V_{\text{cor}}^1 V_2^0 K + V_{\text{cor}}^1 V_1^\infty - V_{\text{cor}}^1 V_2^0$$

$$\alpha_3 = V_{\text{cor}}^1 V_1^\infty K - V_{\text{cor}}^1 V_2^0 K$$

$$\beta_0 = V_{\text{cor}}^1 V_2^0$$

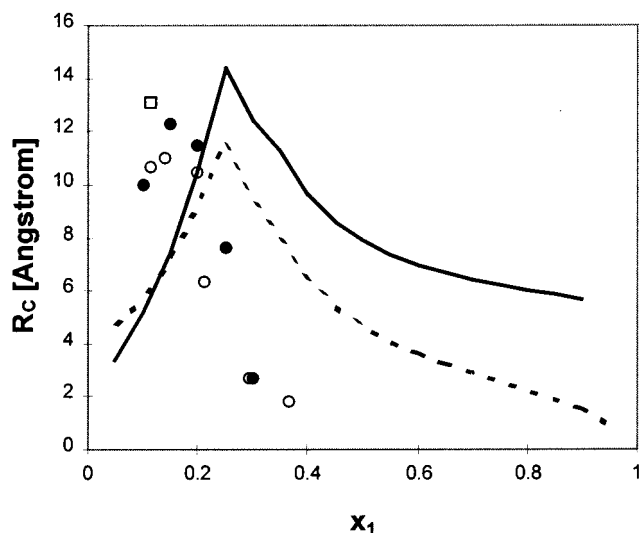
$$\beta_1 = -(V_2^0)^2 K + V_1^\infty V_2^0 K + V_{\text{cor}}^1 V_1^\infty - V_{\text{cor}}^1 V_2^0 + V_{\text{cor}}^1 V_2^0 K$$

$$\beta_2 = (V_2^0)^2 K - V_2^0 V_1^\infty K + V_{\text{cor}}^1 V_1^\infty K - V_{\text{cor}}^1 V_2^0 K$$

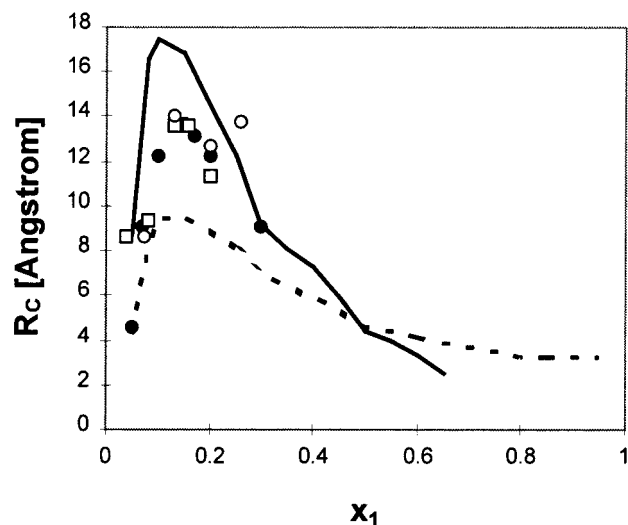
It should be noted that all the above quantities have a linear dependence on  $V_{\text{cor}}^1$ .

## Calculations and Results

The correlation volumes were calculated using eqs 16 and 17 for the aqueous systems 1-PrOH ( $T = 303.15$  K) and *t*-BuOH ( $T = 323.15$  K). These systems were chosen because reliable data about their clustering are available (Table 1). The values of the KBIs were taken from our previous paper,<sup>48</sup> and the



**Figure 1.** Correlation radius  $R_c$  against  $x_1$  for the 1-propanol–water system. The broken line is for the alcohol-rich cluster and the solid line is for the water-rich cluster; experimental data from: ●, ref 15; ○, ref 17; □, ref 19.



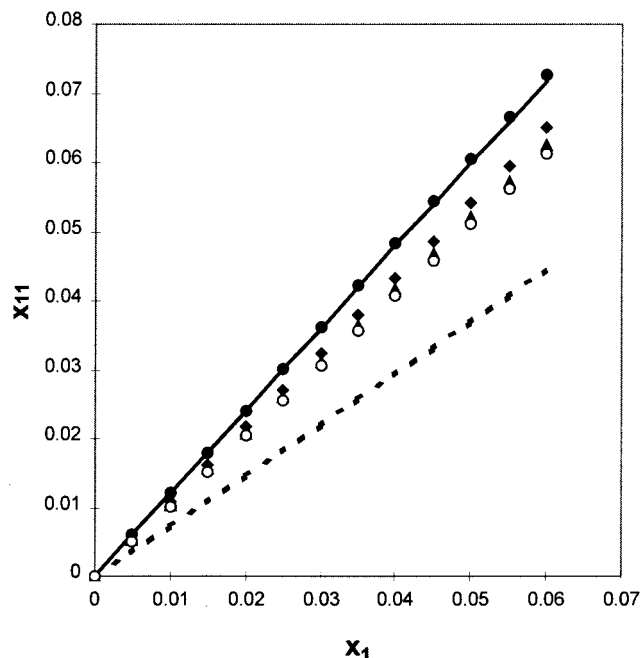
**Figure 2.** Correlation radius  $R_c$  against  $x_1$  for the *tert*-butanol–water system. The broken line is for the alcohol-rich cluster and the solid line is for the water-rich cluster; experimental data from: ●, ref 14 ( $T = 301.15$  K); ○, ref 21 ( $T = 293.15$  K); □, ref 23 ( $T = 293.15$  K).

NRTL equation was used to express  $x_{ij}$  in terms of the overall composition. The parameters of the NRTL equation were taken from the Gmehlings vapor–liquid equilibrium (VLE) data compilation.<sup>58</sup> The results of the calculations are compared with experimental data in Figures 1 and 2.

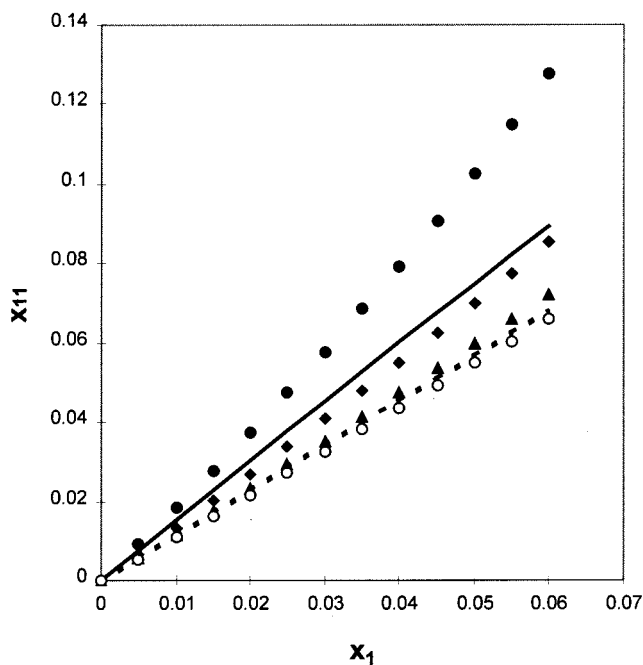
The local composition  $x_{11}$  was calculated with eq 27 for dilute aqueous solutions of MeOH, EtOH, 1-PrOH, 2-PrOH, and *t*-BuOH at 298.15 K in the composition range  $0 \leq x_1 \leq 0.06$ . The partial molar volumes of alcohols at infinite dilution were taken from literature.<sup>2</sup> The parameter  $K(P, T)$  was calculated using data from the Gmehlings VLE compilation.<sup>58</sup> The results are compared with those calculated with the Wilson and the NRTL equations in Figures 3–7. The parameters of the Wilson and NRTL equations were taken from the above-mentioned compilation.<sup>58</sup>

## Discussion

A satisfactory agreement was found between the sizes of the clusters determined experimentally and calculated. For the

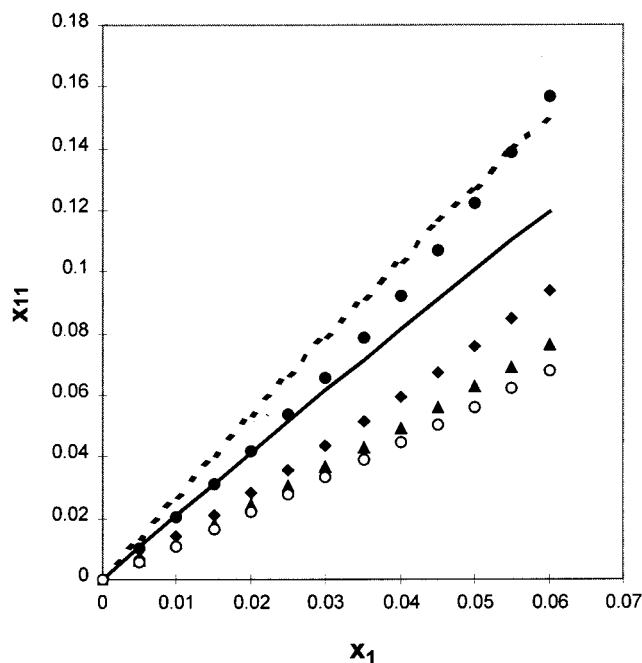


**Figure 3.** Local composition in the methanol–water system. The solid line is calculated with the NRTL and the broken line with the Wilson equation; ●, eq 27 with  $V_{\text{cor}}^1 = 100$  cm<sup>3</sup>/mol; ◆, eq 27 with  $V_{\text{cor}}^1 = 250$  cm<sup>3</sup>/mol; ▲, eq 27 with  $V_{\text{cor}}^1 = 500$  cm<sup>3</sup>/mol; ○, eq 27 with  $V_{\text{cor}}^1 = 1000$  cm<sup>3</sup>/mol.

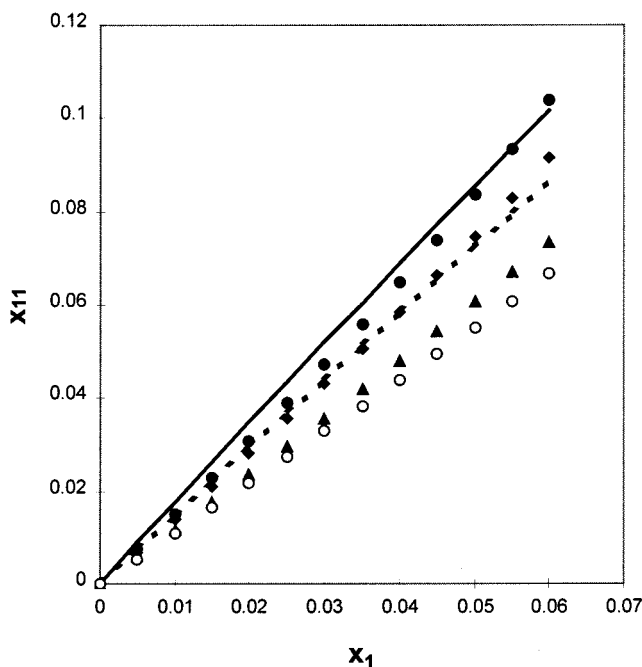


**Figure 4.** Local composition in the ethanol–water system. The solid line is calculated with the NRTL and the broken line with the Wilson equation; ●, eq 27 with  $V_{\text{cor}}^1 = 100$  cm<sup>3</sup>/mol; ◆, eq 27 with  $V_{\text{cor}}^1 = 250$  cm<sup>3</sup>/mol; ▲, eq 27 with  $V_{\text{cor}}^1 = 500$  cm<sup>3</sup>/mol; ○, eq 27 with  $V_{\text{cor}}^1 = 1000$  cm<sup>3</sup>/mol.

1-PrOH + H<sub>2</sub>O solutions, the calculations indicate (Figure 1) that two types of clusters, namely alcohol- and water-rich, are present in the solution and that the dependencies of their sizes on composition are similar. They reach a maximum at an alcohol molar fraction  $x_1 \approx 0.2$ – $0.3$ , after which they decrease. A similar behavior was found for  $\Delta n_{ij}$ .<sup>48</sup> Even though the systems investigated are homogeneous at all compositions (in normal conditions), a “phase separation” at molecular scale, in water-

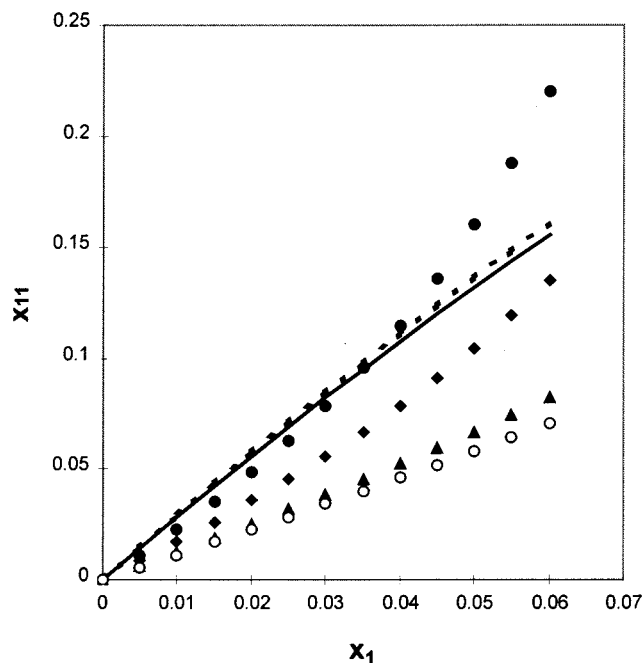


**Figure 5.** Local composition in the 1-propanol–water system. The solid line is calculated with the NRTL and the broken line with the Wilson equation; ●, eq 27 with  $V_{\text{cor}}^I = 100 \text{ cm}^3/\text{mol}$ ; ◆, eq 27 with  $V_{\text{cor}}^I = 250 \text{ cm}^3/\text{mol}$ ; ▲, eq 27 with  $V_{\text{cor}}^I = 500 \text{ cm}^3/\text{mol}$ ; ○, eq 27 with  $V_{\text{cor}}^I = 1000 \text{ cm}^3/\text{mol}$ .



**Figure 6.** Local composition in the 2-propanol–water system. The solid line is calculated with the NRTL and the broken line with the Wilson equation; ●, eq 27 with  $V_{\text{cor}}^I = 100 \text{ cm}^3/\text{mol}$ ; ◆, eq 27 with  $V_{\text{cor}}^I = 225 \text{ cm}^3/\text{mol}$ ; ▲, eq 27 with  $V_{\text{cor}}^I = 500 \text{ cm}^3/\text{mol}$ ; ○, eq 27 with  $V_{\text{cor}}^I = 1000 \text{ cm}^3/\text{mol}$ .

and alcohol-rich clusters, takes place. Although there is qualitative agreement with the experimental results provided by the SAXS and SANS, the calculated values do not decay for  $x_1 > 0.4$  as rapidly as the experimental ones. A similar conclusion can be noted for the system *t*-BuOH + H<sub>2</sub>O (Figure 2). The cluster size combined with the values of  $\Delta n_{ij}$  allow one to estimate the cluster composition. At the molar fraction  $x_1 = 0.1$ , the alcohol composition in the alcohol-rich cluster is 0.145



**Figure 7.** Local composition in the *tert*-butanol–water system. The solid line is calculated with the NRTL and the broken line with the Wilson equation; ●, eq 27 with  $V_{\text{cor}}^I = 100 \text{ cm}^3/\text{mol}$ ; ◆, eq 27 with  $V_{\text{cor}}^I = 175 \text{ cm}^3/\text{mol}$ ; ▲, eq 27 with  $V_{\text{cor}}^I = 500 \text{ cm}^3/\text{mol}$ ; ○, eq 27 with  $V_{\text{cor}}^I = 1000 \text{ cm}^3/\text{mol}$ .

and in the water-rich cluster is 0.096; for  $x_1 > 0.35$ , the alcohol-rich cluster is essentially free of water molecules and the alcohol molar fraction in the water-rich clusters is about 0.14–0.15.

Because the cluster composition is not constant, a clathrate-like structure cannot be used for its representation. Nevertheless, the clathrate-like structure  $[(\text{PrOH})_8(\text{H}_2\text{O})_{40}]$  suggested in ref 20 is compatible with the water-rich clusters for  $x_1 > 0.35$ . Indeed, the alcohol molar fraction of about 0.15, calculated for the water-rich clusters when  $x_1 > 0.35$ , corresponds to the clathrate  $(\text{PrOH})_8(\text{H}_2\text{O})_{40}$ .

The Kirkwood–Buff model can be used for the calculation of the local composition in the dilute region. Our calculation of the local composition in the aqueous systems of MeOH, EtOH, 1-PrOH, 2-PrOH, or *t*-BuOH is compared with the local compositions provided by the Wilson and NRTL equations (Figures 3–7). The local composition of an aqueous solution of MeOH, calculated with eq 27 for  $V_{\text{cor}}^I = 100 \text{ cm}^3/\text{mol}$  (Figure 3), is in agreement with the local composition obtained from the NRTL equation; this means that even if clusters are present in this solution, they are small. (For comparison, the molar volume of pure MeOH in normal condition is  $40.74 \text{ cm}^3/\text{mol}$ .) The local composition of EtOH + H<sub>2</sub>O system plotted in Figure 4 shows that there is agreement between eq 27 and the NRTL equation for  $V_{\text{cor}}^I \approx 250 \text{ cm}^3/\text{mol}$ ; consequently the clusters in this system are also small. There is some experimental evidence that small clusters are present in the EtOH + H<sub>2</sub>O system.<sup>19,28,59</sup> It is worth mentioning that for the systems MeOH + H<sub>2</sub>O and EtOH + H<sub>2</sub>O there is no agreement between the Wilson and NRTL equations. For the 1-propanol–water system and  $x_1 < 0.03$  (Figure 5), there is agreement between eq 27 and the Wilson and NRTL equations for  $V_{\text{cor}}^I \approx 100$ – $250 \text{ cm}^3/\text{mol}$ . The size of the clusters determined experimentally (Table 1) is in agreement with the above values of  $V_{\text{cor}}^I$ . For the 2-PrOH + H<sub>2</sub>O system (Figure 6), small clusters are present in the dilute region. Figure 7 shows that for the system *t*-BuOH + H<sub>2</sub>O, there is quantitative agreement between eq 27 and the



NRTL equation for  $V_{\text{cor}}^1 \approx 100\text{--}175 \text{ cm}^3/\text{mol}$  and  $x_1 < 0.04$ . The latter values of  $V_{\text{cor}}^1$  are in agreement with the SAXS results (Table 1).

## Conclusion

The clustering in aqueous solutions of alcohols was examined by combining the Kirkwood–Buff theory of solution with the Wilson and the NRTL equations. The correlation volumes were calculated for the aqueous systems of 1-PrOH and *t*-BuOH. Two type of clusters, alcohol- and water-rich, were found with similar dependencies of size on composition. Satisfactory agreement was found between the calculated cluster sizes and those provided by the SAXS, SANS, and LS experiments.

An analytical expression was derived for the local composition in the dilute region, which was used for the dilute aqueous solutions of MeOH, EtOH, 1-PrOH, 2-PrOH, and *t*-BuOH. The results were compared with those obtained with the Wilson and NRTL equations and on this basis the correlation volume in the dilute region evaluated. It was found that small clusters (such as dimers and trimers) can be present in the dilute region of alcohols.

## Appendix

The main formulas for the calculation of the KBIs<sup>40,46–47</sup> are

$$G_{12} = G_{21} = RTk_T - \frac{V_1 V_2}{VD} \quad (\text{A1})$$

$$G_{ii} = G_{12} + \frac{1}{x_i} \left( \frac{V_j}{D} - V \right) \quad i \neq j \quad (\text{A2})$$

where

$$D = \left( \frac{\partial \ln \gamma_i}{\partial x_i} \right)_{P,T} x_i + 1 \quad (\text{A3})$$

In eqs A1–A3,  $k_T$  is the isothermal compressibility,  $V_i$  is the partial molar volume of component  $i$ ,  $x_i$  is the molar fraction of component  $i$ ,  $V$  is the molar volume of the mixture, and  $\gamma_i$  is the activity coefficient of component  $i$ .

Consequently, the KBIs of an ideal binary mixture,  $G_{ij}^{\text{id}}$ , are given by the expressions:<sup>40,46,47</sup>

$$G_{12}^{\text{id}} = RTk_T^{\text{id}} - \frac{V_1^0 V_2^0}{V^{\text{id}}} \quad (\text{A4})$$

$$G_{11}^{\text{id}} = G_{12}^{\text{id}} + V_2^0 - V_1^0 \quad (\text{A5})$$

and

$$G_{22}^{\text{id}} = G_{12}^{\text{id}} - (V_2^0 - V_1^0) \quad (\text{A6})$$

where  $k_T^{\text{id}}$  and  $V^{\text{id}}$  are the isothermal compressibility and the molar volume of an ideal mixture, respectively, and  $V_i^0$  is the molar volume of the pure component  $i$ .

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