

Structures of Alkyl Benzoate Binary Mixtures. A Kirkwood–Buff Fluctuation Theory Study Using UNIFAC

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Received: April 29, 2005; In Final Form: August 20, 2005

The structure of the alkyl benzoate + *n*-alkane, and + alkan-1-ol binary mixtures were analyzed according to the Kirkwood–Buff fluctuation theory on the basis of both the mixture properties measured over a wide temperature range and the activity coefficients calculated with the modified UNIFAC (Dortmund) model as well. Application of this model reveals that both the microheterogeneous structure and the clustering effects are strongly dependent on the chain length of the *n*-alkane and alkan-1-ol cosolvents. Knowledge of the local composition around each type of molecule is drawn from the Kirkwood–Buff integrals and the excess (or deficit) molecules aggregated around a central one. The rather high values of the integrals evaluated for some of these systems provide first-hand evidence for phase splitting. The conclusions drawn support previous analyses and confirm the adequacy of the methodology put forward for studying liquid mixtures at microscopic level; easily measurable experimental properties can advantageously be used with the fluctuation theory.

Introduction

Benzoic acid esters, alkyl benzoates, are useful compounds with interesting applications. The easily polarizable π -electron system confers these compounds a highly selective solvent ability in the separation of polar from nonpolar compounds as well as a dipolar and hydrophobic character which make them adequate solvents for a number of technological applications.¹ Alkyl benzoates often are used as fragrances and antibacterial agents in cosmetic formulations, as plasticizers in the manufacture of key poly(vinyl chloride) (PVC) polymers, and as textile dye carriers for the treatment of synthetic fibers, among others. However, despite these promising applications, so far there is available only a scant literature on the properties and structure of these solvents, either pure or mixed. This work continues the ongoing research on binary and ternary ester-containing mixtures; previously, we have reported on a number of thermophysical properties from which valuable microscopic information was inferred.^{2–5}

The macroscopic behavior of liquids can be attributed to different microscopic effects, and not always is easy to discern which microscopic property is the source of a particular macroscopic observation. Therefore, drawing microscopic level conclusions on solvent structure on the basis of the thermophysical properties often is questionable and must be performed carefully to reach a fair connection between both approaches; otherwise, erroneous or simplified interpretations may arise. This mismatch can be overcome by applying statistical mechanics models capable of connecting reliably the microscopic and macroscopic approaches. Among the different models available, the Kirkwood–Buff fluctuation theory constitutes quite a useful tool in applying statistical mechanics to practical thermodynamic problems.⁶ Although the original version of the model has enabled the obtaining of thermodynamic properties from radial distribution functions using the so-called Kirkwood–Buff integrals, unfortunately such functions still are not well-known for most systems; therefore, application of this theory often is

not feasible for systems of interest in industry. However, after the work by Ben-Naim, the methodology was inverted;⁷ that is, since these integrals may provide information on both the local environment and the preferential solvation effect, the Kirkwood–Buff integrals evaluated with the properties measured can be reliably used to draw conclusions on solution structure. This proposal makes application of the model feasible in an exact manner without introducing any assumptions and thus opens a new route to the theory; also, it has given rise to an efficient tool to investigate solution structure and local molecular environment by linking macroscopic properties with microscopic level analyses.⁸

In this work the Kirkwood–Buff integrals and the local composition of alkyl benzoate + *n*-alkane, and + alkan-1-ol binary mixtures have been calculated at different temperatures. The properties needed are the partial molar volumes and isothermal compressibility values reported in previous works as well;^{2–5} activity coefficients are also needed, and these were calculated according to the modified UNIFAC (Dortmund) model.⁹ Application of the Kirkwood–Buff theory requires very accurate values of the properties used; hence, application of UNIFAC activity coefficients may enable obtaining reliable results.

Methods

The Kirkwood–Buff theory is a rigorous statistical mechanics model that has provided a plausible route to evaluate thermodynamic properties from microscopic structure. The G_{ij} Kirkwood–Buff integrals (KBIs),⁶ are defined as

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

where g_{ij} is the radial distribution function of the species *i* around a central *j* molecule in the grand canonical (μVT) ensemble, and *r* is the distance between the centers of the two molecules. KBIs can be regarded as a certain normalized measure of the tendency of the *i* molecules to cluster around a central *j*

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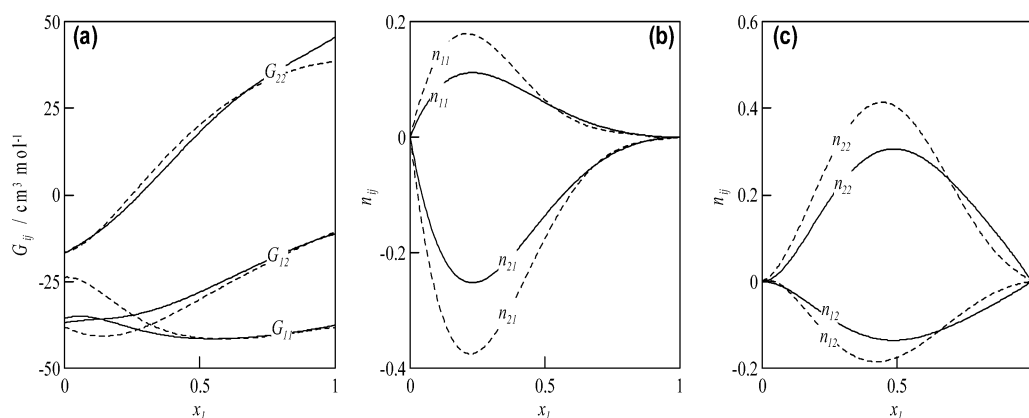


Figure 1. x_1 methanol + $(1 - x_1)$ water system at 298.15 K: (a) G_{ij} Kirkwood-Buff integrals; excess (or deficit) molecules around (b) a central methanol molecule, (c) a central water molecule. Key: continuous lines, values obtained in this work; dashed lines, values from Ruckenstein and Sulgic¹¹ at 313.15 K.

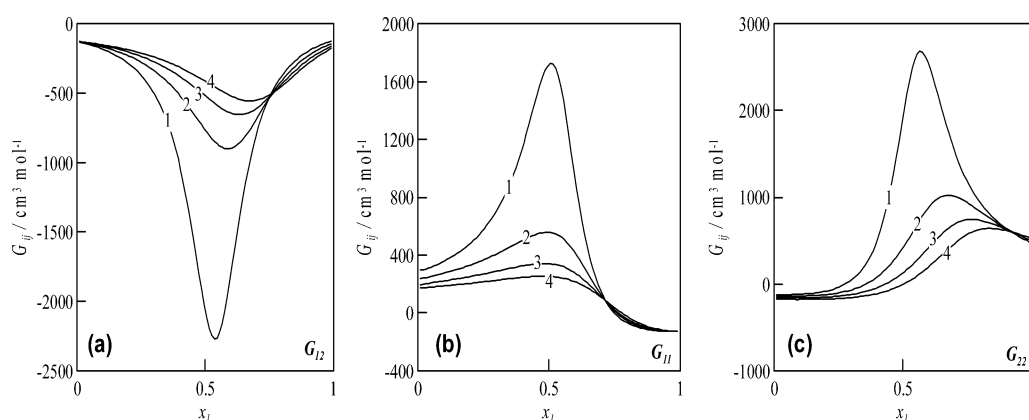


Figure 2. G_{ij} Kirkwood-Buff integrals for x_1 n -hexane + $(1 - x_1)$ alkyl benzoate binary systems at 298.15 K. The figures indicate the m values ($m = 1, 2, 3$, and 4) of the alkyl chain length of alkyl benzoate.

molecule.⁸ The role played by the radial distribution function in the definition of the G_{ij} integrals along with the inclusion of KBIs in the equations for several thermodynamic properties reflects well the connection of microscopic structure with macroscopic thermodynamic properties through the linkage of KBIs.¹⁰

The inverted method developed by Ben-Naim enables the obtaining of KBIs from a number of thermodynamic properties at a fixed temperature: activity coefficients, partial molar volumes and isothermal compressibilities. Evaluation of KBIs from thermodynamic data requires introducing no assumptions; hence, the microscopic information obtained from these analyses appears fully reliable. Deviations of mixed solvents from the ideal behavior often can be explained by the so-called preferential solvation, that is, the difference in composition of the solvent shell of a solute molecule compared to the bulk solvent. The excess (or deficit) molecules around a central one, n_{ij} , can be evaluated from the corresponding KBIs; however, to interpret consistently such values and to suitably obtain a fair description of the solution structure in systems prone to intermolecular interactions, a proper system must be selected as the reference level and its KBIs subtracted from the KBIs of the system investigated. Therefore, the symmetrical ideal solution, which can be regarded as nonaggregated¹⁰ and whose KBIs differ from zero, has been chosen as the reference level;¹¹ hence, the difference between the integrals of this state and those of a nonideal system can in principle be attributed to intermolecular

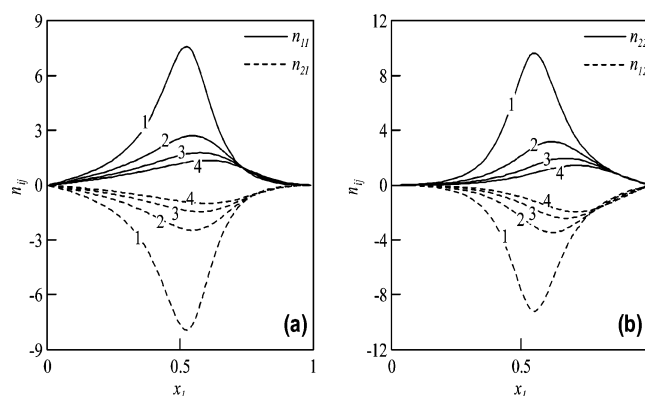


Figure 3. x_1 n -hexane + $(1 - x_1)$ alkyl benzoate binary systems at 298.15 K: Excess or deficit molecules around (a) a central n -hexane molecule and (b) a central alkyl benzoate molecule; m values as in Figure 2.

effects, and the excess (or deficit) molecules around a central one can be calculated according to

$$n_{ij} = c_i \Delta G_{ij} = c_i (G_{ij} - G_{ij}^{\text{IDEAL}}) \quad (2)$$

where c_i is the molar concentration of the component i . A number of equations useful to calculate KBIs values in

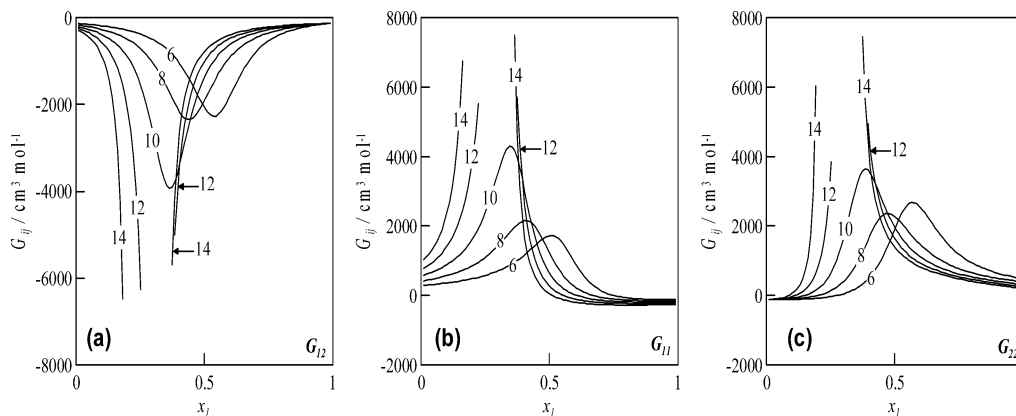


Figure 4. G_{ij} Kirkwood–Buff integrals for x_1 n -alkane + $(1 - x_1)$ MB binary systems at 298.15 K. The figures indicate the n values ($n = 6, 8, 10, 12$ and 14) of the n -alkane chain length.

binary systems from thermodynamic data are available, eqs 3–7.^{10,12}

$$G_{ij} = RTk_T - \frac{\bar{V}_i \bar{V}_j}{VD} \quad (3)$$

$$G_{ii} = G_{ij} + \frac{1}{x_i} \left(\frac{\bar{V}_j}{D} - V \right) \quad (4)$$

where R denotes the universal gas constant, V the molar volume and \bar{V}_i the partial molar volume of the i th compound. The KBIs for ideal binary systems are calculated according to

$$G_{ij}^{\text{IDEAL}} = RTk_T^{\text{IDEAL}} - \frac{V_i V_j}{V^{\text{IDEAL}}} \quad (5)$$

$$G_{ii}^{\text{IDEAL}} = G_{ij}^{\text{IDEAL}} + (V_j - V_i) \quad (6)$$

where V_i is the molar volume of the i th compound.

The partial molar volumes previously reported for the alkyl benzoate + n -alkane or + alkan-1-ol systems at different temperatures were calculated according to the intercept method from the molar excess volumes evaluated from density measurements.^{2,3} The contribution of the isothermal mixture compressibility, RTk_T , to most Kirkwood–Buffs integrals is almost negligible and becomes noticeable only for small KBIs.¹³ Thus, the isothermal compressibilities were evaluated from the values of the pure components by linear interpolation with respect to volume fractions. The third property required, the activity coefficient derivatives with composition, normally are evaluated from the isothermal vapor–liquid equilibria (VLE) data, and are introduced in the KBIs through the D function

$$D = 1 + x_i \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{P,T} \quad (7)$$

The error analysis performed in the evaluation of the KBIs indicates that these functions are very sensitive to experimental uncertainties;^{14,15} the main source stems from the mathematical differentiation needed both to derive the D functions with eq 7 and to calculate the partial molar volumes from the sets of molar excess volumes data-pairs. The uncertainty in the activity coefficients has quite a pronounced effect on the D and KBIs values; hence, erroneous activity coefficient fittings may yield meaningless asymptotic values at both the low and high composition limits.¹⁴ In short, very accurate and thermodynamically consistent activity coefficients must be employed; for

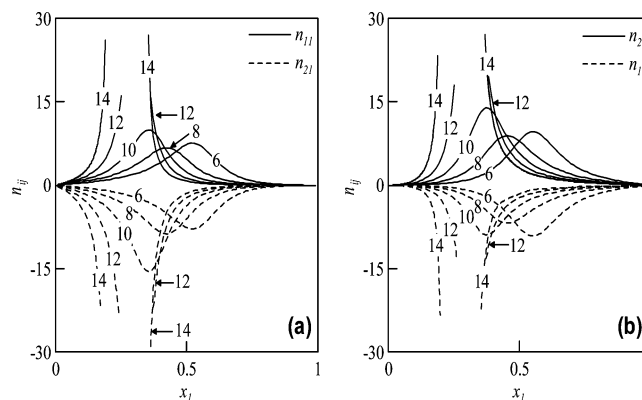


Figure 5. x_1 n -alkane + $(1 - x_1)$ MB binary systems at 298.15 K. Excess (or deficit) of molecules is shown (a) around a central n -alkane molecule and (b) around a central MB molecule; n values are as in Figure 4.

instance, the requirement that the D function be always positive is imposed by the thermodynamic stability condition. However, if only low-precision VLE data are available, then negative D values may arise; that is, thermodynamically inconsistent data may lead to uncertain KBIs. For systems in the boundary of the mixture phase separation the D values obtained are close to zero, with the added effect that very small errors in the activity coefficients may result in large errors in the KBIs evaluated.¹⁶ In summary, quite a critical factor in KBIs calculation is the proper choice of the most efficient combination of VLE and molar excess volume data which, to provide accurate KBIs, should be thermodynamically consistent.

So far the thermodynamic consistency of an appreciable amount of the VLE literature data consulted does not seem to be well verified; therefore, use of such data to calculate KBIs without prior checking might be hazardous. Furthermore, collecting VLE data is quite a costly, time-consuming task,¹⁷ and reliable results are obtained only if well-defined protocols are followed.¹⁸

In this work, the obtaining of activity coefficients and their composition derivatives by the modified UNIFAC (Dortmund) model is suggested.⁹ This model has proved to yield very accurate values for a number of mixture properties,^{19–21} such accuracy being supported by the quite large highly accurate databases from which the group parameters are obtained; modified UNIFAC is included in most process simulator packages and is widely used in the chemical industry both in process design and in thermophysical properties calculation. The reliable partial molar volumes deduced from the densities measured by vibrating tube densitometry^{2–5} combined with the

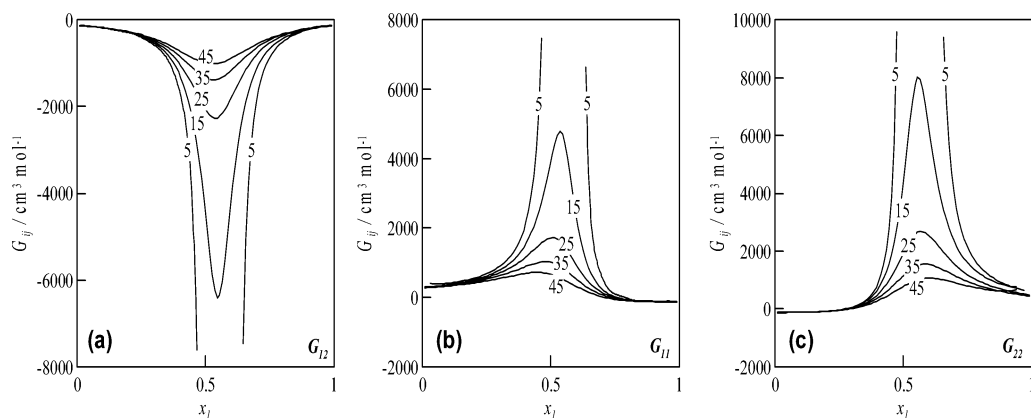


Figure 6. G_{ij} Kirkwood–Buff integrals for x_1 *n*-hexane + $(1 - x_1)$ MB binary systems at different temperatures. The figures indicate temperature in °C.

activity coefficients evaluated from the modified UNIFAC group parameters available, yielded accurate and reliable KBIs.

The reliability of this procedure was verified by comparison of the KBIs and n_{ij} functions calculated for the strongly nonideal x_1 methanol + $(1 - x_1)$ water system with those available in the literature. A recent survey on methanol–water KBIs data demonstrates that the KBIs collected from different sources neither quantitatively nor qualitatively agreed.¹³ In this work, the KBIs values for methanol–water mixtures at 298.15 K, calculated using the molar excess volumes from Bai and Han²² and the activity coefficient derivatives evaluated with the modified UNIFAC model⁹ are compared with those by Ruckenstein and Sulgin at 313.15 K,¹¹ who reported a rigorous and consistent analysis and highly reliable functions as well; the KBIs and n_{ij} values show a fair agreement (quantitative and qualitative) within a reasonable margin of error (Figure 1) despite the different temperatures used.

Other different literature methods available are based on properties other than VLE data. For instance, molecular dynamics simulations in the grand canonical ensemble^{23,24} may yield quite accurate KBIs, but the computational effort is too high so as to perform a systematic study. KBIs calculated from X-ray²⁵ or neutron scattering²⁶ data also enable to derive accurate functions, but these costly techniques are not commonly available; although quite a simple alternative method based on density and ultrasonic measurements has also been reported, so far the results are not accurate enough to deduce reliable molecular level information.²⁷

In conclusion, the method put forward in this work to determine KBIs and the derived functions appears accurate enough, so that molecular level conclusions can be drawn with ease of experimental performance, low computational effort, and sufficient reliability. The KBIs and derived functions for alkyl benzoate + *n*-alkane or + alkan-1-ol binary systems were calculated from the molar excess volumes and isothermal compressibilities reported,^{2,3} and the activity coefficients derivatives calculated from the modified UNIFAC (Dortmund) group parameters obtained from Gmehling et al.⁹

Results and Discussion

The Kirkwood–Buff analysis is split into two sections. In the first section the KBIs and n_{ij} functions for the x_1 *n*-alkane + $(1 - x_1)$ alkyl benzoate binary mixtures are determined over the full composition range from 278.15 to 318.15 K and in 10 K steps. The solvents studied are the even *n*-alkanes, from *n*-hexane to *n*-tetradecane, mixed with methyl benzoate (MB), ethyl benzoate (EB), propyl benzoate (PB), and butyl benzoate

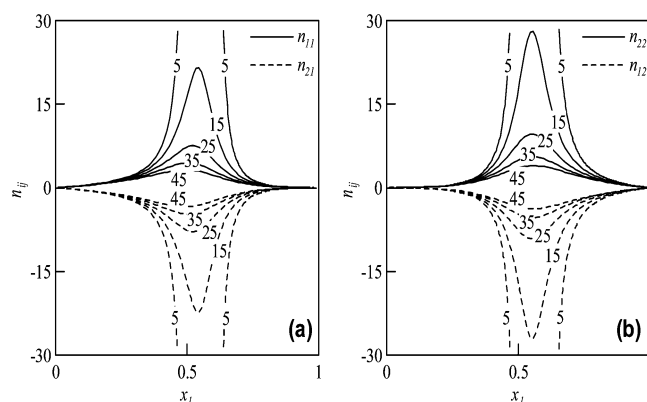


Figure 7. x_1 *n*-hexane + $(1 - x_1)$ MB binary systems at different temperatures. Excess (or deficit) molecules is shown around (a) a central *n*-hexane molecule and (b) a central MB molecule. The figures indicate temperature in °C.

(BB). To confirm previously reported conclusions, the study deals with the analyses of the *n*-alkane chain length, *n*, alkyl benzoate chain length, *m*, and temperature effects on the functions and molecular level structure. Second, the functions for the x_1 alkan-1-ol + $(1 - x_1)$ alkyl benzoate binary mixtures at 298.15 K are determined over the full composition range. The mixtures studied are the set of alkan-1-ols, from methanol to undecan-1-ol, and the above alkyl benzoates, with the objective of analyzing the alcohol chain length, *p*, ester chain length, *m*, and temperature effects on the KBIs and derived properties. Likewise, the intermolecular hydrogen bonding effect is analyzed according to the derived functions. Finally, a comparison of the properties of the *n*-alkane and alkan-1-ol containing systems is also undertaken.

***n*-Alkane—Alkyl Benzoate Binary Systems.** The G_{ij} and n_{ij} functions for the *n*-hexane + alkyl benzoate binary systems at 298.15 K (Figures 2 and 3) show the alkyl chain effect. The large negative G_{12} values (Figure 2a) and positive G_{11} and G_{22} values (Figures 2b,c) point to a somewhat modest affinity between *n*-hexane and the alkyl benzoates, the KBIs decreasing in absolute value with increasing *m*. By far the hexane molecules become preferentially solvated by hexane molecules and the alkyl benzoates by alkyl benzoate molecules. The large KBI values denote large solvation radii, even larger than those of the first coordination sphere.²⁸

The MB molecules are essentially dipolar and planar in shape; these features give rise to a very effective packing effect, confirmed by the large densities.^{2,5} Addition of hexane causes no disruption of such an ordering; the linear *n*-alkane molecules are excluded from the planar packing of the MB molecules,

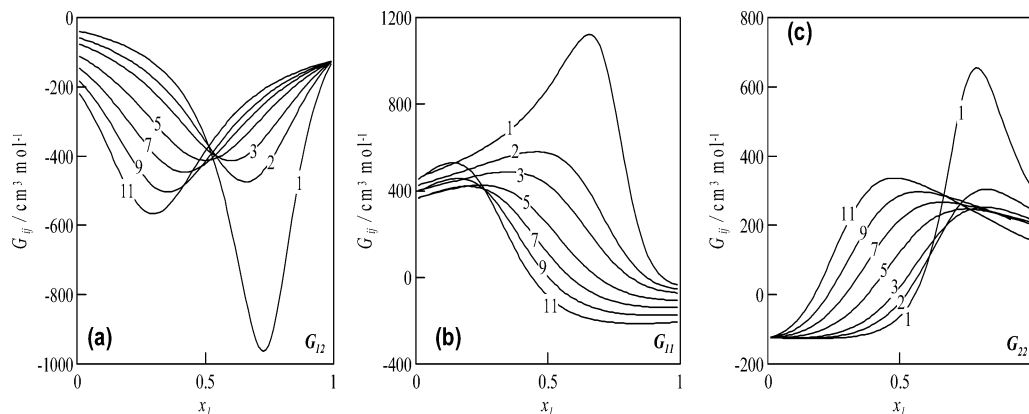


Figure 8. Kirkwood–Buff integrals, G_{ij} , in the x_1 alkan-1-ol + $(1 - x_1)$ MB binary systems at 298.15 K. The figures indicate the p values ($p = 1, 2, 3, 5, 7, 9$, and 11) of alkan-1-ols chain length.

which tend to be surrounded by n -alkane molecules. This observation is confirmed by the large positive n_{ii} functions, in contrast with the large negative n_{ij} values (Figure 3). The ester planarity decreases as the alkyl benzoate chain length is raised,³ and the ordering brought about by the effective packing of the ester molecules also decreases; yet a somewhat more randomly molecular distribution appears, although the preferential solvation for large esters still remains.

The variation of KBIs with increasing m shows a complex behavior, in particular in the high hexane mole fraction regions (Figure 2). At high hexane concentrations, the G_{11} integrals shift to negative values and the preferential solvation vanishes; therefore, alkyl benzoate is the component that determines the mixture structure. For low alkyl benzoate concentrations, an almost random mixing occurs, with the result being a local composition close to the bulk composition. The maxima and/or minima of the functions at (roughly) equimolar composition shift to higher mole fractions with increasing m , this feature demonstrating that the alkyl benzoate structure determines the molecular level distribution.

Figures 4 and 5 show the alkane chain length effect. An increase in the n values is accompanied by an increase in the KBIs and n_{ij} functions; that is, if the n -alkane chain length increases for the same ester, then the affinity between the two components drops. The quite large values obtained for the upper n -alkanes somehow reflect the relative closeness of the mixture to the phase separation limit;¹⁶ this effect is also revealed by the close to zero D function and justifies the decision to only partly show the curves for upper n -alkanes. In summary, the preferential solvation raises as n increases and promotes an incipient phase instability. This feature suggests that the observed trend to like–like preferential solvation is brought about by the dispersive interactions between the hydrocarbon-like moieties, which increases as the n -alkane chain length is raised.²⁹ Furthermore, the observed shift to lower n -alkane mole fractions of the maxima and minima reported indicates that the preferential solvation appears even in the low concentration regions. The notable difference in size and shape of the n -alkanes and esters studied gives rise to steric effects that noticeably increase as the n values increase. For short n -alkanes, the ester and n -alkane sizes become closer; therefore, at low n -alkane concentrations, a certain degree of a more efficient packing between the two components may emerge. At equimolar compositions, such a packing effect becomes weakened with increasing n -alkane mole fraction, giving rise to large KBIs and preferential like–like solvation. For upper n -alkanes, the difference in size and shape with the esters stepwise increases, and the ester packing effect becomes increasingly inefficient

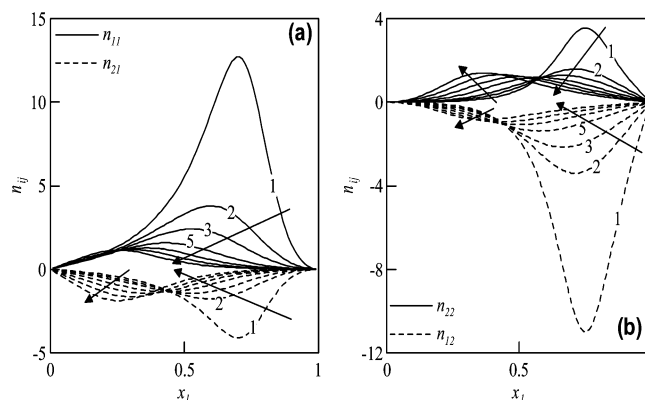


Figure 9. x_1 alkan-1-ol + $(1 - x_1)$ MB binary systems at 298.15 K. Excess (or deficit) of molecules is shown around (a) a central alkan-1-ol molecule and (b) a central MB molecule. The figures indicate the p values, as in Figure 8, and the arrows indicate increasing p values ($p = 1, 2, 3, 5, 7, 9$, and 11).

even at low n -alkane concentrations; as a result, the maxima and minima of the functions shift to lower concentrations. For instance, the molar volume of pure n -tetradecane is twice as that of MB, an effect extremely important in absence of unlike interactions. Thus, the alkyl benzoate structure appears to be incompatible with that of the upper n -alkanes, even at low n -alkane concentrations.

Figures 6 and 7 show the temperature effect on the G_{ij} and n_{ij} functions. The large negative G_{ij} integrals changed to even more negative with decreasing temperature, whereas the positive G_{ii} functions increased with decreasing temperature. This effect reflects a pronounced preferential solvation over the temperature range studied, and it could be the reason for the phase splitting at low temperatures, consistent with the large KBIs values (Figure 6). Because of the thermal molecular motion, a temperature increase results in a decrease in the preferential solvation, an observation supported by the low n_{ij} functions, which makes the formation of like–like solvation spheres difficult; likewise, the observed decrease in the KBIs values at high temperatures is accompanied by a less compact alkyl benzoate packing, which enables the interstitial introduction of n -alkane molecules. The location of the maxima and minima of these functions is almost temperature-independent; that is, the preferential solvation occurs under equimolar conditions and becomes weakened with increasing temperature; hence, the number of coordination spheres decreases approaching the local composition to the bulk composition.

The above conclusions concur with previous studies.^{2,3} The molar excess volumes shifted from negative to positive values

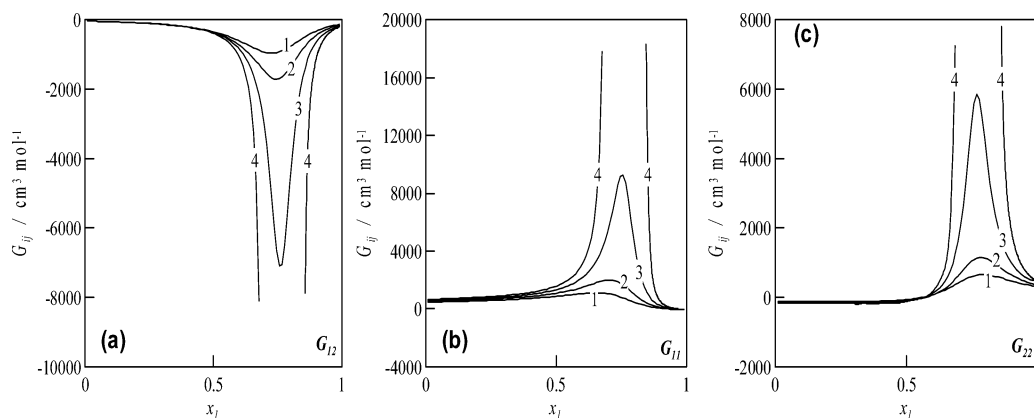


Figure 10. G_{ij} Kirkwood–Buff integrals in the x_1 methanol + $(1 - x_1)$ alkyl benzoate binary systems at 298.15 K. The figures indicate the m value ($m = 1, 2, 3$, and 4) as in Figure 2.

with an increase in the n -alkane chain length, an observation in good agreement with the low KBIs and n_{ij} functions deduced for low n values, and with the quite large values and strong preferential solvation for the upper n values as well. The excess enthalpies for these binary systems were positive throughout, and increase as n increases.²⁸ Also this observation agreed well with the trend shown by the KBIs as the preferential solvation increases; interactions between n -alkane and alkyl benzoates are less likely since unlike molecules are almost absent in the solvation sphere, giving rise to a strong endothermic mixing that increases as n increases. The molar excess volumes and excess enthalpies decreased with increasing m , in full agreement with the shorter KBIs reported in Figure 2;^{2,30} this feature supports the pronounced steric effects that stem from the different size and shape of both types of molecules.

Alkan-1-ol—Alkyl Benzoate Binary Systems. Figures 8 and 9 show the alkan-1-ol chain length effect, p , on the KBIs and n_{ij} functions for the alkan-1-ol + MB binary systems at 298.15 K. The behavior of the methanol + MB binary system differed from that of the other mixtures; its G_{12} functions show a deep minimum at $x_1 \approx 0.7$ and also a very high maximum for G_{11} and G_{22} functions at (roughly) the same mole fraction; therefore, each component of this system becomes preferentially solvated by like molecules. This preferential solvation is extended to further several molecular diameters and drops at low methanol concentrations. The smaller methanol size favors the interstitial accommodation into the ester structure, a conclusion also supported by the negative partial molar excess volumes of this system; this fitting facilitates the formation of H-bonding heteroassociations between the ester CO group and the proton of the alcohol. The strong minima and maxima observed at $x_1 \approx 0.7$ indicate that at high methanol concentration the alcohol structure remains almost unchanged upon ester addition; the alcohol and ester shapes give rise to solvation spheres with deficit of unlike molecules (Figure 9). Thus, the strong minima of excess volumes around $x_1 \approx 0.7$ may be explained by the reordering upon mixing and further fitting of the structures due to their different molar volumes ($V_2 \approx 3V_1$).³ Although establishing methanol–MB cross-association is in principle feasible, such an effect becomes important only at low alcohol mole fractions. As the alcohol concentration increases, the structures of pure solvents remain almost unchanged, and only reorientation effects within the like-solvation shells become likely.

The variation of the functions with increasing p indicates quite a complex behavior. The G_{12} minima shifted to lower alcohol concentration; first the minima decreased in absolute value and

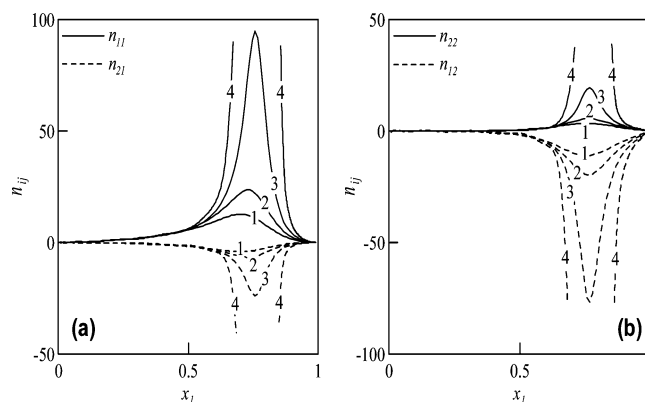


Figure 11. x_1 methanol + $(1 - x_1)$ alkyl benzoate binary systems at 298.15 K. Excess (or deficit) molecules is shown around (a) a central methanol molecule and (b) a central alkyl benzoate molecule. The figures indicate the m value ($m = 1, 2, 3$, and 4) as in Figure 2.

afterward the minimum increased for pentanol; the same effect is observed for the positive G_{11} and G_{22} values. Thus, preferential like solvation is present for all alkan-1-ols studied, but it is less important as p increases; for high alcohol concentrations, G_{11} and G_{22} shifted to negative values and a more random mixture structure appears. The observed shifts of the maxima and minima of the KBIs to ester-rich compositions indicate that for increasing p values the size and shape of both molecules become progressively more different and addition of a small amount of alcohol does not affect the structure of the ester solvation sphere. The excess or deficit molecules around a central one, Figure 9, show a complex behavior. If the alkan-1-ol is regarded as the central molecule, then the local and bulk compositions become closer as p increases, and only at low alcohol concentration is a certain preferential solvation observed. The same effect is reported when the ester is regarded as central molecule; when the alcohol chain length increases, the preferential solvation becomes less important. The positive molar excess volumes for the upper alkan-1-ols indicate that the steric effect arising from disruption of the structure of both components without further heteroassociations effectively determines the structure of this system, with an almost randomly structure as the chain length increases.

The ester chain length effect on KBIs and n_{ij} is plotted in Figures 10 and 11 for methanol + alkyl benzoate mixtures; the locations of the maxima and minima of KBIs as m increases remain almost constant and increase in absolute value, giving rise to very large values for BB. The same behavior is observed

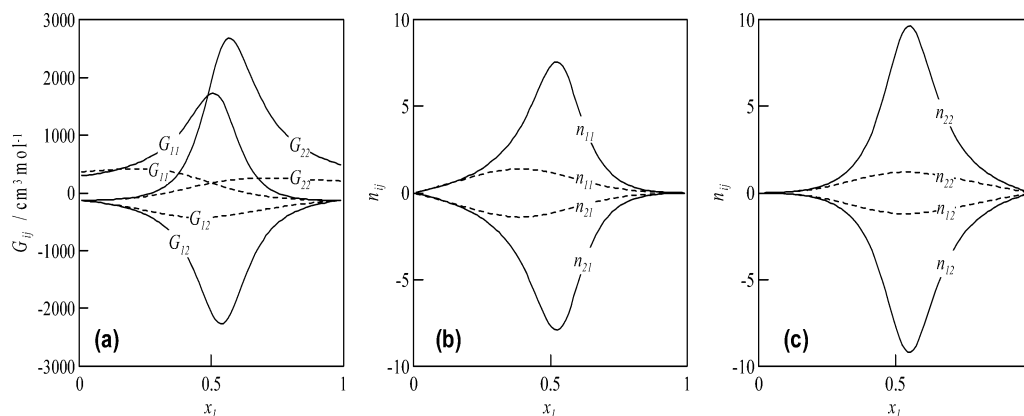


Figure 12. x_1 (*n*-hexane or hexan-ol) + $(1 - x_1)$ alkyl benzoate binary systems at 298.15 K: (a) Kirkwood–Buff integrals, G_{ij} , and excess (or deficit) molecules around (b) a central *n*-hexane or hexan-1-ol molecules and (c) a central MB molecule. Continuous lines are shown for the *n*-hexane-containing system and dashed lines for the hexanol-containing system.

for the excess or deficit molecules around a central one; hence, the preferential solvation is more important as the alkyl chain increases, the radii of the solvation spheres increase, and the local composition becomes quite different from the bulk composition, in good agreement with the decreasing molar excess volumes.³ In summary, for alkan-1-ol–alkyl benzoate, the preferential solvation is rather important, the local composition by far differs from the bulk composition, and the solvation spheres contain quite a large excess of like molecules, which makes establishing heteroassociations difficult; only for methanol in diluted concentrations are heteroassociations likely. The steric effect arising from the different size and shape of alcohols and alkyl benzoates determines the structure of such mixtures.

Comparative Analysis between *n*-Alkane and Alkan-1-ol + Alkyl Benzoate Binary Systems. Figure 12 comparatively plots the KBIs and n_{ij} functions for (*n*-hexane or hexan-1-ol) + MB binary mixtures. The functions show that preferential solvation is more important for the alkane-containing system, their functions being four times higher. The maxima and minima are better defined for the hexane-containing mixtures and its solvation spheres have larger radii. The microheterogeneity arising from the well-defined local compositions is quite important for the *n*-hexane-containing system. In the alcohol mixture, the structure appears to be more random, and the solvation spheres have small radii.

Conclusions

The methodology put forward in this work enables a reliable evaluation of Kirkwood–Buff integrals and the derived properties with enough accuracy to draw molecular level conclusions from easily measurable thermophysical properties. The data analyses connect macroscopic properties with molecular level structures and support the conclusions discussed. Application to alkyl benzoate–*n*-alkane and –alkan-1-ol binary mixtures confirms the conclusions reported, showing that the structure of these mixtures is determined by strong preferential like–like solvation, a feature especially remarkable in *n*-alkane-containing mixtures with structures close to the phase separation. For alkan-1-ol mixtures, heteroassociations by H-bonding are feasible only for methanol at low alcohol concentrations.

Acknowledgment. The financial support by Junta de Castilla y León, Project BU10/03, and MCyT, Project PPQ2002-02150 (Spain), is gratefully acknowledged.

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