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Thermodynamics of 1-alkanol+aromatic compound mixtures. Systems with dimethylbenzene, ethylbenzene or trimethylbenzene

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Abstract

Binary mixtures of 1-alkanols and ethylbenzene, dimethylbenzenes or trimethylbenzenes have been studied in the framework of the DISQUAC model. The interaction parameters for the hydroxyl/aromatic contacts are reported. DISQUAC represents well a set of thermodynamic properties: vapor-liquid equilibria (VLE), liquid–liquid equilibria (LLE), molar excess enthalpies (H^E) and the concentration–concentration structure factor ($S_{CC}(0)$). The model predicts correctly H^E of 1-alkanol+1,4-dimethylbenzene+cyclohexane systems using binary parameters only, that is neglecting ternary interactions. The available database on H^E and molar excess volume (V^E) is examined in order to gain insight into the interactions present in the studied mixtures: (i) dipolar interactions are stronger in systems with benzene; (ii) interactions between unlike molecules decrease with the increase of the chain length of the 1-alkanol for solutions with a given aromatic hydrocarbon; (iii) self-association of 1-alkanols is more important in systems with alkylbenzenes than in those including benzene; (iv) benzene is a more active molecule than other aromatic compounds when breaking the alcohol structure.

Keywords: Alkylbenzene; 1-Alkanol; Association; Dipolar interactions; Structure

1. Introduction

Mixtures containing oxygenated compounds, such as ethers and alkanols are of great importance from a practical point of view. For example, they have been increasingly used as an additive to gasoline owing to their octane-enhancing and pollution-reducing properties [1,2]. However, in the last years, it has been shown that MTBE (methyl tert-butyl ether, a very common additive to gasoline) produces some environmental effects by penetrating through the soil and entering in the groundwater, which is then undesirable for human consumption [3]. For this reason, ethanol is now being added to gasoline [3]. On the other hand, aromatic hydrocarbons are very important constituents in petroleum and gasoline fluids. The addition of self-associated compounds, as alcohols, to such fluids build very complex mixtures. A better knowledge, from both experimental and theoretical points of view, of simplified mixtures, as 1-alkanol+aromatic hydrocarbon systems, is needed to provide improved models which can represent gasoline fluids under various working conditions. On the other hand, the theoretical treatment of alcoholic solutions is also a very interesting matter due to the number of different factors which contribute to the values of their thermodynamic properties: (i) self-association of the alcohols [4]; (ii) change in the extent and strength of the hydrogen bonding when the mixture is formed [4]. So, in systems with a polar or polarizable second compound, H-bonds between unlike molecules are created [4–9]. In the case of 1-alkanol+benzene, or +1,4-dimethylbenzene mixtures, studies on apparent dipole moments of such solutions suggest the existence of linear trimers[7,8]. The difference between $H_1^{E,\infty}$ (excess molar partial enthalpy at infinite dilution of the alcohol) for ethanol+*n*-alkane (25.2 kJ mol^{-1}) [10] and for ethanol+benzene, or +toluene (≈16 kJ mol^{-1} [11]) has been interpreted as a consequence of the mentioned interactions between unlike molecules [9]. For 1-alkanol+amine systems, the O–H…N bonds between the alkanol and the amine are even stronger than the O–H…H bonds between alkanol molecules [12]. (iii)

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Physical contributions and (iv) structural effects [13]. The values of the excess properties result from balances between these contributions, and their relative importance depends on the property under consideration [4,13,14].

1-Alkanol+aromatic compound mixtures have been investigated in terms of different association theories, with physical interactions represented by equations such as Scatchard-Hildebrand, NRTL or UNIQUAC [15–21]. An important result is that some of these theories are able to describe not only thermodynamic data but also spectroscopy data [15,20]. The quasichemical generalized model proposed by Barker [22] has been applied rather successfully to some mixtures of this kind [22,23]. In the framework of the Dortmund UNIFAC group contribution model [24], interaction parameters for mixtures containing benzene, toluene or ethylbenzene are available. However, no interaction parameters have been reported for mixtures for di or trialkylbenzenes.

The purpose of this article is to investigate 1-alkanol+alkylbenzene (ethylbenzene, xylenes or trimethyllbenzenes) mixtures in the framework of DISQUAC [25], a purely physical model based on the rigid lattice theory developed by Guggenheim [26]. In order to gain a deeper insight into the interactions and structures characteristics of these mixtures, they are also studied in terms of the so-called concentration–concentration structure factor, $S_{CC}(0)$ [27]. We have shown elsewhere that DISQUAC is a reliable tool to describe this important property [28–30]. In this way, we continue a systematic research on alcoholic solutions using DISQUAC. So, previously, we have studied, among others, systems such as 1-alkanol, +benzene, +toluene [31,32], +tetrachloromethane [33], +ketone [34], +carbonate [35], +ester [36], +monocarboxylic acid [37], or +amine [38]). We have also shown that DISQUAC provides very accurate predictions on VLE and H^E for ternary systems, even for those with alcohols, neglecting ternary interactions, i.e., using binary parameters only [39,40].

2. Theory

2.1. DISQUAC

In the framework of DISQUAC, 1-alkanol+alkylbenzene mixtures are regarded as possessing the following three types of surface: (i) type a, aliphatic (CH_3, CH_2, in alkylbenzenes or 1-alkanols; (ii) type b, C_6H_5, C_6H_4; or C_6H_3 in alkylbenzenes; (iii) type h, hydroxyl (OH in 1-alkanols).

2.1.1. General equations

The main features of DISQUAC are: (i) the total molecular volumes, r_i, surfaces, q_i, and the molecular surface fractions, α_i, of the compounds present in the mixture are calculated additively on the basis of the group volumes R_G and surfaces Q_D recommended by Bondi [41]. As volume and surface units, the volume R_{CH4} and surface Q_{CH4} of methane are taken arbitrarily [42]. The geometrical parameters for the groups referred to in this work are given elsewhere [43,44]. (ii) The partition function is factorized into two terms, in such way that the excess functions are calculated as the sum of two contributions: a dispersive (DIS) term which represents the contribution from the dispersive forces; and a quasichemical (QUAC) term which arises from the anisotropy of the field forces created by the solution molecules. In the case of G^E, a combinatorial germ, $G^{E,COMB}$, represented by the Flory–Huggins equation [42,45] must be considered. Thus

$$G^E = G^{E,COMB} + G^{E,DIS} + G^{E,QUAC} \quad (1)$$

$$H^E = H^{E,DIS} + H^{E,QUAC} \quad (2)$$

(iii) The interaction parameters are assumed to be dependent on the molecular structure; (iv) The value $z=4$ for the coordination number is used for all the polar contacts. This represents one of the more important shortcomings of the model, and is partially removed via the hypothesis of considering structure dependent interaction parameters.

The equations used to calculate the DIS and QUAC contributions to G^E and H^E in the framework of DISQUAC are given elsewhere [43]. The temperature dependence of the interaction parameters is expressed in terms of the DIS and QUAC interchange coefficients [43], $C^{DIS}_{st,l}$; $C^{QUAC}_{st,l}$ where $s \neq t$ are two contact surfaces present in the mixture and $l=1$ (Gibbs energy); $l=2$ (enthalpy), $l=3$ (heat capacity).

2.2. Concentration–concentration structure factor

Mixture structure can be studied using the $S_{CC}(0)$ function [27], defined as [27,46,47]:

$$S_{CC}(0) = \frac{RT}{(\partial^2 G^M/\partial x_1^2)_{P,T}} = \frac{x_1 x_2}{D} \quad (3)$$

with

$$D = \frac{x_1 x_2}{RT}(\partial^2 G^M/\partial x_1^2)_{P,T} = 1 + \frac{x_1 x_2}{RT}\left(\frac{\partial^2 G^E}{\partial x_1^2}\right)_{P,T} \quad (4)$$

D is function closely related to thermodynamic stability [46,48]. For ideal mixtures, $G^{E,id}=0$; $D^{id}=1$ and $S_{CC}(0)=x_1x_2$. As stability conditions require, $S_{CC}(0)>0$, and if the system is close to phase separation, $S_{CC}(0)$ must be large and positive (∞, when the mixture presents a miscibility gap). In contrast, if compound formation between components appears, $S_{CC}(0)$ must be very low (0, in the limit). So, if $S_{CC}(0)>x_1x_2$, i.e., $D<1$, the dominant trend in the system is the separation of the components (homocoordination), and the mixture is less stable than the ideal. If $0<S_{CC}(0)<x_1x_2=S_{CC}(0)^{id}$, i.e., $D>1$, the fluctuations in the system have been removed, and the dominant trend in the solution is compound formation (heterocoordination). In this case, the system is more stable than ideal.

3. Estimation of the DISQUAC interaction parameters

The three surfaces, a, b, h present in the studied systems generate three types of contacts: (a,b); (a,h) and (b,h). The interaction parameters of the (a,b) contacts are purely dispersive and have been determined previously on the basis of experimental