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A MODEL OF CHEMICAL ASSOCIATION IN BINARY MIXTURES

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Abstract

A general model of chemical association is presented for the correlation of activities of components of a binary mixture A + B with negative deviation from Raoult's law. The model takes into account the coexistence in solution of the species A, B, AB and AB_2. The model is applied to the mixture of propanone-trichloromethane, resulting in a satisfactory correlation of the activities. For this system the deviation from ideality can be explained simply by the formation of the AB complex, with $\Delta_{ass,1} H^o$ = (-1.2±0.4) kJ mol^{-1} and $\Delta_{ass,1} S^o$ = (-34±1) J K^{-1} mol^{-1}, as the standard enthalpy and entropy of association for the hydrogen bond formation in this system.

Key words: Thermodynamics, non-ideal mixtures, liquid-vapour equilibrium.

Palabras clave: Termodinámica, mezclas no-ideales, equilibrio líquido-vapor.

I. Introduction

Association or attractive interaction between components of a mixture is the origin of negative deviations from Raoult's law. These interactions commonly result from hydrogen bonding between the components, leading to formation of complexes or associated species.

Three principal theoretical approaches for the study of the non–ideal behaviour of solutions are chemical, quasi-chemical and perturbation methods. [1]

A classical instance of a non–ideal solution is the mixture of propanone and trichloromethane, which involves strong interactions between these molecules. Such a condition has stimulated interest in this system, which has accordingly become the object of numerous investigations, thus demonstrating the formation of associated species through hydrogen bonding. [2] Amongst experimental evidence that the interactions give rise to the formation of a binary complex (Figure 1a) are solid–liquid

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phase diagrams, [3,4] and indications in ^{1}H-NMR or IR spectra of the existence of hydrogen bonds. [5,6] The formation of such an associated species explains negative values in excess thermodynamic functions, but several authors have suggested the formation of a ternary complex (Figure 1b), [2,7,8] due to lack of mixing thermodynamic functions in the composition region rich in chloroform. [2]

Chemical models are more conceptual from a molecular point of view than other models, for the understanding of negative deviations from Raoult's law. Historically, the first chemical approach for the study of non–ideality in liquid mixtures was applied by Dolezalek; [9] Harris subsequently modified that theory. [10]

I offer hereby a chemical model of association: such a model yields mathematical expressions for the correlation of activities of propanone and trichloromethane with the standard enthalpy and entropy of association as parameters. This model is similar to that of Apelblat, [11] but it is considered as a process of successive association mechanism: the coexistence of whichever of the following species: A, B, AB and AB_2.

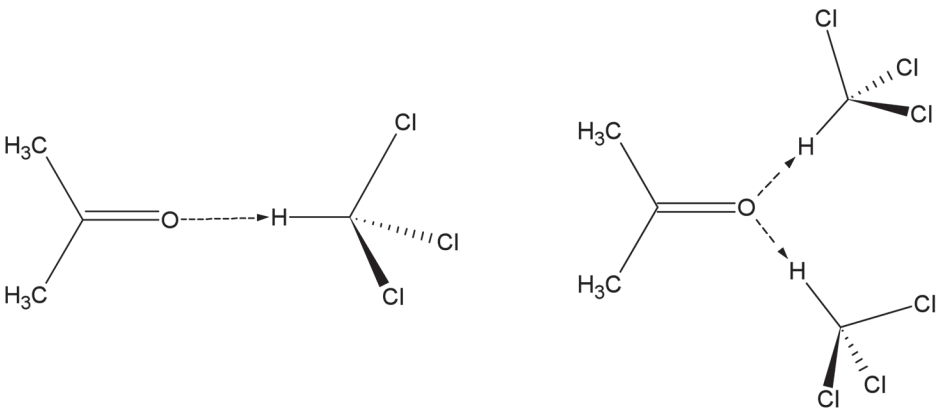

Figure 1. Postulated complexes involving propanone and trichloromethane.

Theory of the model of chemical association

Consider the association of two substances A and B (propanone and trichloromethane, for example) to occur by the following mechanisms, as Durov and Shilov described, [2]

$$A + B \overset{K_1}{\rightleftharpoons} AB \qquad (1)$$

$$AB + B \overset{K_2}{\rightleftharpoons} AB_2 \qquad (2)$$

in which steps (1) and (2) are consecutive. The ternary complex in step (2) must thus be preceded by formation of the binary complex in step (1); a proposal that is

different the one of McGlashan and Rastogi. [12] The binary mixture hence supports the coexistence of species of types A, B, AB and AB_2. The deviations from ideality of those mixtures reflect precisely the strong interactions that cause the formation of the associated species.

The thermodynamic equilibrium constants for each association process are given by:

$$K_1 = \frac{a_{AB}}{a_A a_B} \tag{3}$$

$$K_2 = \frac{a_{AB_2}}{a_A a_B} \tag{4}$$

The total amount of coexisting species is

$$N_T = N_A + N_B + N_{AB} + N_{AB_2} \tag{5}$$

The molar fractions N_i / N_T are considered to equal activities a_i of species in solution, because such fractions take into account the associative interactions responsible for deviations of the mixtures from ideality. Hence

$$a_i = \frac{N_i}{N_T} \tag{6}$$

and the sum of activities of all the species present in the mixture must be:

$$a_T = a_A + a_B + a_{AB} + a_{AB2} = 1 \tag{7}$$

Equations (3) and (4) imply that: $a_{AB} = K_1 a_A a_B$ and $a_{AB} = K_2 a_{AB} a_B = a_{AB} = K_1 K_2 a_A a_B^2$. Making these substitutions into equation (7), one finds that:

$$a_A = \frac{1 - a_B}{1 + K_1 a_B + K_1 K_2 a^2} \tag{8}$$

where the thermodynamic equilibrium constants vary with the temperature T:

$$K_i = \exp\left(-\frac{\Delta_{ass,i} H^{\ominus}}{RT} + \frac{\Delta_{ass,i} S^{\ominus}}{R} \right) \tag{9}$$

for i =1, 2. R is the gas constant. The equation obtained by substitution of equation (9) into equation (8) allows the fitting of the activities of A and B at different temperatures,

with the standard enthalpy of association $\Delta_{ass,i}\ H^o$and the standard entropy of association $\Delta_{ass,i}\ S^o$ for each association step i, as correlation parameters.

II. Materials and method

The following cases are considered:

1. Simple association, considering $K_1 > 0$, and $K_2 = 0$.

2. Double association, considering $K_1 > 0$, and $K_2 > 0$.

Calculation of the standard parameters of association.

The activities of the species A (propanone) and B (trichloromethane) are calculated in a conventional manner, from liquid–vapour equilibrium data at constant temperature (liquid composition x_i, vapour composition y_i and vapour pressure of the mixtures p):

$$a_i = \frac{y_i p}{p_i^0} \tag{10}$$

in which i = A, B; p_i^0 is the vapour pressure of the pure component i, or at constant pressure (liquid composition x_i , vapour composition y_i and boiling temperature). In this latter case, the p_i^0 at each temperature was calculated using Clausius-Clapeyron equation.

The data of activities a_A and a_B at the different compositions and temperatures are fitted to the model obtained by the combination of equations (8) and (9), with a computational algorithm for non–linear plots (Maple 7®). Data for liquid-vapour equilibrium were taken from reference [13].

III. Results and discusion

The data for the system propanone-trichloromethane are plotted at several compositions and temperatures as shows the Figure 2.

The surface in Figure 2 was obtained assuming $K_2 = 0$, and the parameters were the standard enthalpy of association $\Delta_{ass,1}\ H^o$ = (–11.2±0.4) kJ mol^{-1} and the standard entropy of association $\Delta_{ass,1}\ S^o$ = (–34±1) J K^{-1} mol^{-1}, with a variance of the fit of $\sigma^2 = 1.2 \times 10^{-4}$, ($\sigma_2 = \sum_i \delta^2_i / (N_{dat} - N_{par})$, with residuals δ_i, N_{dat} of data points and N_{par} parameters). This enthalpy value agrees with those reported in the literature [2, 7, 14].

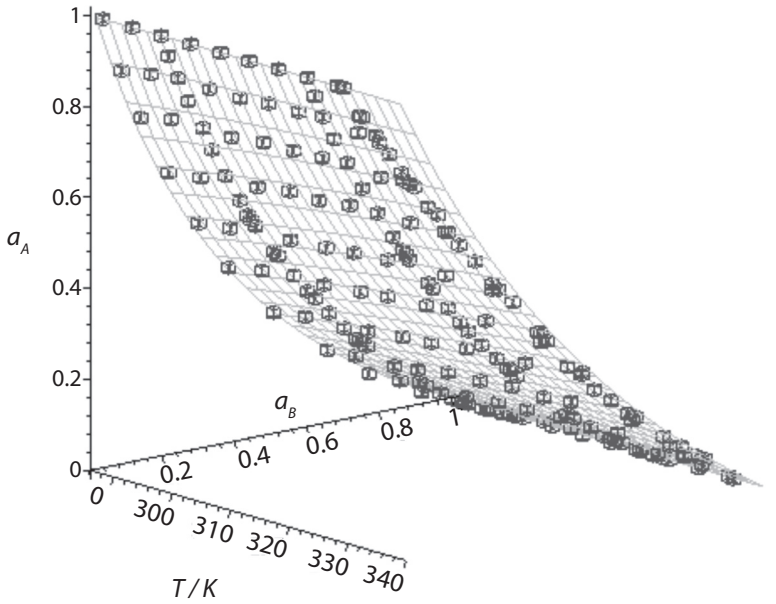

Figure 2. Fit of the activities of propanone (A) and trichloromethane (B) at several temperatures according to equations (8) and (9), assuming simple association.

Taking in account the second associating process where the ternary complex AB_2 is formed, the following parameters were found: $\Delta_{ass,1} H^o = (-11 \pm 2)$ kJ mol^{-1}, $\Delta_{ass,1} S^o = (-35 \pm 4)$ J K^{-1} mol^{-1}, $\Delta_{ass,2} H^o = (-13 \pm 10)$ kJ mol^{-1} and $\Delta_{ass,2} S^o = (-58 \pm 5)$ J K^{-1} mol^{-1}. The enthalpy and entropy for the simple association are reproduced, but the parameters for the second association process have enormous confidence intervals. A possible explanation for this result is that the second process of association occurs to a small extent. No evidence of this formation of a ternary complex has arisen from analysis of cooling curves or spectra. Nevertheless, this model of double association is considered reasonable from an intuitive molecular point of view, because of the two pairs of non-bonded valence electrons of the oxygen atom of propanone.

Using the Akaike's criterion of information *AIC*, which is related to the entropy of information, [15] ($AIC = N_{dat} \ln((\sum_i \delta^2_i / N_{dat}) + 2N_{dat} N_{par} (N_{dat} - N_{par} - 1))$ for the comparison of the two models (simple association *versus* simple + double associations), one finds that the simple association model is better (lower *AIC*) for the explanation of the deviation from ideality in mixtures of propanone and trichloromethane.

IV. Conclusions

The model of chemical association described here satisfactorily correlates activities of components in the binary real system propanone + trichloromethane. The model

enables the calculation of equilibrium constant for the association. The variation with temperature of K_1 for this system is consistent with a standard enthalpy of association (-11.2±0.4) kJ mol^{-1}. This value conforms to other values in the literature [2, 7, 14]. The standard entropy of association for this system is (-34±1) J K^{-1} mol^{-1}. A second association step for the formation of the AB_2 complex is not well established, due to large uncertainties in the enthalpy and entropy values for this process. The Akaike's information criterion favours the model of simple AB association as sufficient interpretation of the data. This result is reasonable in molecular terms, because of the expected lack of stability of two hydrogen bonds bound to a single carbonyl oxygen.

V. Aknowledgements

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