

Thermodynamics of Molecular Interactions in Butyl Acetate + Benzene or Toluene Mixtures in terms of an Ideal Associated Solution Model

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1. Introduction

Alkyl esters are characterized by dipole-dipole interactions in the pure state [1]. The additions of inert solvents like alkane generally break the orientation order of pure alkyl esters to give the positive value of excess thermodynamic functions. However, these values become very less and even negative in the mixtures of alkyl esters + aromatic hydrocarbons [2] due to the presence of specific interactions of dipole-induced dipole type. In our earlier paper [3], the analysis of V^E and H^E data for n-butyl acetate + cyclohexane or benzene or toluene suggests that butyl acetate in pure state exists as associated entity and $(i + j)$ mixtures are characterized by the presence of $(i - j)$ molecular entity. In this paper, excess molar Gibbs free energies of mixing (G^E) calculated from the measured VLE data for n-butyl acetate + cyclohexane or benzene or toluene at 308.15 ± 0.01 K. The G^E values were also interpreted in terms of ideal associated model.

2. Experimental

Butyl acetate, cyclohexane, benzene and toluene (Merck) were purified by standard methods [4]. The total vapor pressures of the pure components and their various binary mixtures were measured as a function of liquid phase mole fraction of butyl acetate (x_A) at 308.15K by the static method [5]. The values of excess molar Gibbs free energies of mixing G^E as a function of composition are calculated from VLE data using Barker's method.

3. Results and discussion

The G^E and H^E data at 308.15 K were combined to give TS^E values, which are positive for cyclohexane and toluene systems and negative for benzene system. At the simplest qualitative level the observed H^E and G^E data for these mixtures, may be accounted for if we assume that (i) there are n- π specific interactions between carbonyl group of butyl acetate and π -cloud of benzene and toluene ring and (ii) there is disruption in the dipole-dipole interactions in butyl acetate and the orientational order of other pure components.

As the effect of factor (i) is missing in cyclohexane + butyl acetate mixtures, therefore TS^E is positive, showing the increase in the orientational freedom in these mixtures. It is further supplemented by the high positive value of H^E for the same system. For benzene + butyl acetate system; the TS^E values are found to be negative, showing more orientational order in these mixtures. Also slightly negative values of H^E for these mixtures shows the predominance of factor (i) over factor (ii).

The H^E and G^E values for toluene + butyl acetate system are negative and TS^E values are positive showing the presence of factor (i) & (ii) but the factor (ii) outweigh the effect due to factor (i).

The H^E and activity coefficient data for these mixtures have been analyzed in terms of an ideal associated model [6]. It is assumed that in a binary solution of butyl acetate (A) and benzene or toluene (B) there is a mutual equilibrium of species $A_m B_n$:



The equilibrium constants for the various associated reactions represented by Eq. (1) are:

$$K_{m,n} = a_{A_m B_n} / a_A^m \cdot a_B^n \quad (2)$$

where “ a ” denotes the activities. If sum of the activity coefficients of the various species represented in Eq. (1) are assumed to be unity the material balance equation for the system can be written as

$$a_A + a_B + \sum K_{m,n} a_A^m \cdot a_B^n = 1 \quad (3)$$

we next considered two cases (i) $m = n = 1$ and (ii) $m = 1, 2$ and $n = 1$. Thus equation (3) reduces to Eqs. (4) and (5) for cases (i) and (ii) respectively.

$$(1 - a_A - a_B)/a_B = K_{11} a_A \quad (4)$$

$$(1 - a_A - a_B)/a_A a_B = K_{11} + K_{21} a_A \quad (5)$$

The observed activities of the components of these binary mixtures were corrected for the dispersion contributions using the expressions

$$a_A = \gamma_A x_A / \gamma_A^* \quad \text{and} \quad a_B = \gamma_B x_B / \gamma_B^* \quad (6)$$

where γ_A^* and γ_B^* are the activity coefficients of butyl acetate (A) + cyclohexane (B). Fig. 2 shows plot of $(1 - a_A - a_B)/a_A a_B$ versus a_A yielded a straight line (Fig. 1), except some points fell off the line below $a_A \approx 0.15$.

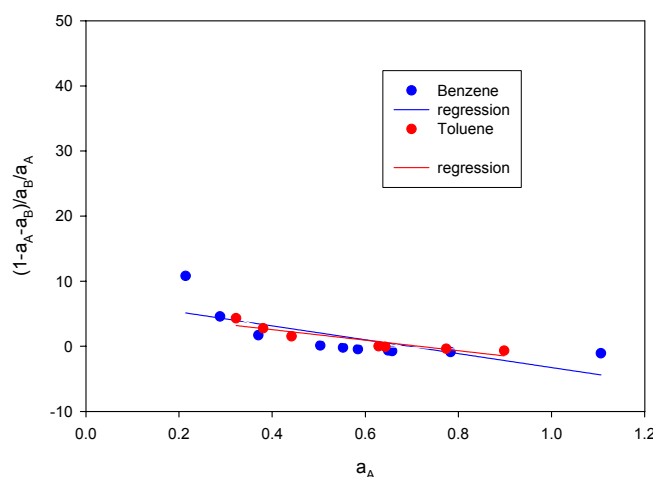


Figure 1. Calculation of K_{11} and K_{21}

This suggests that these mixtures may be assumed to have AB and A_2B molecular species in the solution. The K_{11} and K_{21} were evaluated from the intercept and slope of line and are given in Table 1.

Table 1. Values of K_{11} , K_{21} , ΔH_{11} and ΔH_{21} parameters

System	K_{11}	K_{21}	ΔH_{11} (kJ mole ⁻¹)	ΔH_{21} (kJ mole ⁻¹)
Butyl acetate+benzene	3.2	5.06	-4.881	-1.662
Butyl acetate+toluene	3.45	2.56	-7.733	5.582

Examination of H^E data of the above mentioned mixtures at 308.15 K in terms of case (ii), required that H^E may be expressed as:

$$H^E = [n_{AB}\Delta H_{11} + n_{A_2B}\Delta H_{21}] / (N_A + N_B) \quad (7)$$

where n_{AB} and n_{A_2B} are the amounts of species AB and A_2B present at equilibrium in the solution and N_A and N_B are stoichiometric amounts of A and B and ΔH represents the enthalpy of formation of various molecular species present in these mixtures. If the equilibrium mole fraction of A, B, AB and A_2B are represented by z_A , z_B , z_{AB} , and z_{A_2B} , then for an ideal associated mixture $A+B$ containing AB and A_2B molecular species

$$z_A + z_B + z_{AB} + z_{A_2B} = 1 \quad (8)$$

$$\text{where } z_{AB} = K_{11}z_Az_B \quad \text{and} \quad z_{A_2B} = K_{21}z_A^2z_B \quad (9)$$

The experimental H^E values were again corrected for dispersion contributions by subtracting the H^E values for butyl acetate (A) + cyclohexane (B) system from H^E exptl, at 308.15 K. Consequently

$$H^E = H_{\text{exptl}}^E - H_{\text{butylacetate+cyclohexane}}^E \quad (10)$$

Algebraic manipulation [7] of Eqs. (7)-(9) and material balance equations

$$N_A = n_A + n_{AB} + 2n_{A_2B} \quad \text{and} \quad N_B = n_B + n_{AB} + n_{A_2B} \quad (11)$$

leads to

$$H^E (1 + K_{11}z_A + K_{21}z_A^2) / z_A(1 - x_A) = K_{11}\Delta H_{11} + K_{21}\Delta H_{21}z_A \quad (12)$$

Further combination of Eqs. (8), (9) and (11) leads to

$$x_A = [(1 + K_{11})z_A + K_{21}z_A^2(2 - z_A)] / [1 + K_{11}z_A(2 - z_A) + K_{21}z_A^2(3 - 2z_A)] \quad (13)$$

The values of ΔH_{11} and ΔH_{21} were calculated from the slope and intercept of *L.H.S.* versus z_A (Fig.2) and recorded in Table 1. Using K_{11} , K_{21} , ΔH_{11} and ΔH_{21} values in Eq. (12), values of H^E at different mole fractions were obtained and compared with the corresponding H^E experimental values in Fig.3.

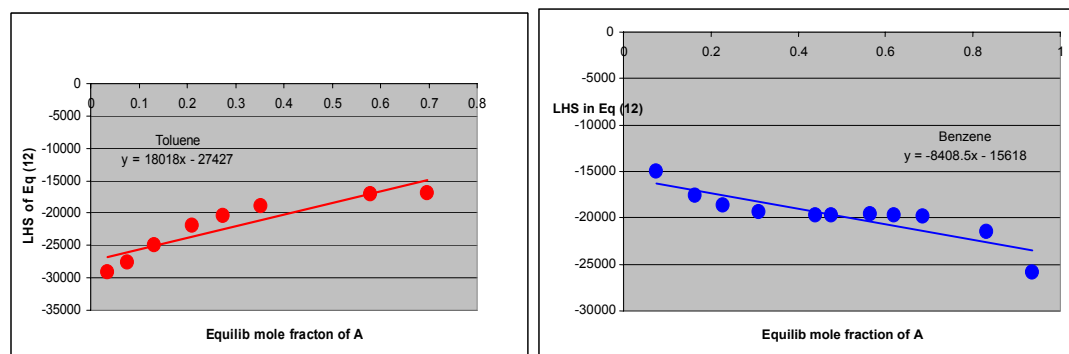


Figure 2. Plot of $H^E (1 + K_{11}z_A + K_{21}z_A^2) / z_A(1 - x_A)$ versus z_A

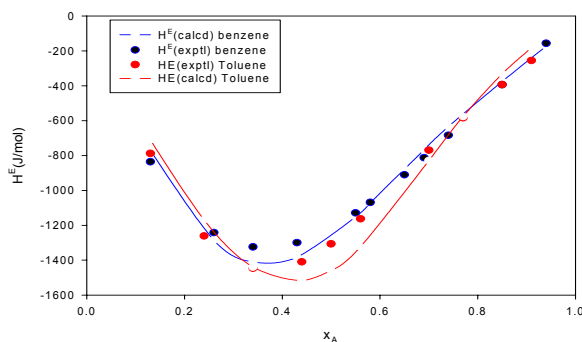


Figure 3. Comparison of experimental and calculated H^E

Thus, the analyses of the H^E and G^E data for butyl acetate + benzene or toluene mixtures suggests that these mixtures are characterized by the presence of AB and A_2B molecular species predominantly. The presence of other molecular species like A_2B_2 , A_3B etc., if at all present, do not contribute significantly to the over all H^E values.

4. References

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