

## Thermodynamic properties of the S/L interfacial layer: Stabilization of the colloidal system in binary liquids

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**Abstract** - In the knowledge of the adsorption and wetting properties of solid particles the influence of particle-liquid and interparticle interaction has been examined on the stability and structure formation of suspensions obtained for hydrophobic  $\text{SiO}_2$  colloids in the mixtures benzene+n-heptane and methanol+benzene. The Hamaker constants of the adsorption layer of composition range. The Hamaker constant have been determined by optical dispersion measurements in the entire mixture composition range. The Hamaker constant of the adsorption layer of composition different from that in the bulk have been calculated at several mixture compositions on the basis of the adsorption results. Having the excess isotherms available enabled us to determine the adsorption layer thickness as a function of the bulk composition. For interparticle attractive potentials, model calculations have been effected on the basis of the Vincent model. In the case of hydrophobic particles dispersed in benzene+n-heptane and methanol+benzene mixtures it was established that the change of the attractive potential was in accordance with the interactions obtained from rheological measurements.

### INTRODUCTION

Rheological, adsorption and immersional wetting of solid particles formed by highly-dispersed hydrophobic silica have been discussed separately in a number of publications. Our previous work (ref. 1) pointed out a close relation between rheological parameters characteristic to the structure formation of a suspension and the composition of the adsorption layer. It was found, that in a certain composition range, i.e. in the environment of the adsorption azeotropic point the free energy minimum of the adsorption layer results in optimal wetting (lyosorption) and the corresponding dispersion stability. The results of optical density measurements of mixture series pointed out the importance of dispersion interactions in binary liquids. There must be an important relation between the polarizability of the dispersed particles and the dispersion medium and accordingly, between the optical properties and the attractive potential.

In the present study we examined the thickness of the adsorbed layer (lyosphere) on the surface of particles and the layer thickness as a function of the mixture composition based on the adsorption excess isotherms. For the characterization of the interaction on the solid-liquid interface the free energy of wetting was calculated according

to the Gibbs equation. For binary mixtures, the enthalpy of wetting was also obtained by microcalorimetric measurements. The Hamaker constants of the mixture series were calculated, and taking the selective adsorption into account, the Hamaker constants of the adsorbed layers, different from that of the bulk phase were also presented. Considering the interfacial layer, calculations of the attractive potential were carried out on the basis of the Vincent model (refs. 2,3). The influence of the lyosphere was investigated in terms of the change in the potential function with mixture composition.

### ADSORPTION AND WETTING IN BINARY LIQUIDS

Adsorption layer formation occurs on the surface of particles dispersed in liquid phase due to the interactions of the solid-liquid interface. The composition of the adsorption layer,  $x_i^s$  is different from both the initial and the equilibrium compositions,  $x_i^0$  and  $x_i$  respectively.

In the case of a solid-liquid interface, having the excess isotherm available, the integrated form of the Gibbs equation makes it possible to calculate the excess free energy of the adsorption layer as a function of the bulk phase composition (refs. 6-9)

$$\Delta_{21}G = - \int_{a_1=0}^{a_1} (n_1^{\sigma(n)} / x_2 a_1) da_1 \quad (1)$$

where  $n_1^{\sigma(n)} = f(x_1)$  the adsorption excess isotherm. The activity  $a_i = f_i x_i$  can be calculated according to the Redlich-Kister equation (refs. 9-11).

The shape of the enthalpy of wetting isotherms determined in binary mixtures is closely associated with the type of the excess isotherms (U or S type). This suggests that the enthalpy isotherm  $\Delta_w H = f(x_i)$  is essentially determined by the composition of the interfacial layer ( $n_i^s, x_i^s$ ) (ref. 12).

The difference between the volume fraction of the adsorption layer  $\phi_i^s$  and that of the bulk phase ( $\phi_i$ ) calculated from the adsorption layer model is (ref. 13):

$$\phi_i^s - \phi_i = n_1^{\sigma(n)} V_{m,j} / V^s (x_i + r^* x_j) \quad (2)$$

where  $V_{m,i}$  is the molar volume of component  $i$ ,  $r^* = V_{m,j} / V_{m,i}$  is the ratio of the molar volumes of the mixture components, and  $V^s$  is the adsorbed layer volume. According to the expression  $t^s = V^s / a^s$ , the thickness of liosphere can be obtained from the above equation as follows:

$$t^s = (n_1^{\sigma(n)} V_{m,j} / a^s x_i) [\phi_i / (\phi_i^s - \phi_i)] \quad (3)$$

where  $a^s$  is the specific surface area of the particles. The layer thickness calculated this way may be approximately constant as a function of the mixture composition, but it may also change significantly with the bulk composition.

### CALCULATION OF THE HAMAKER CONSTANTS IN THE ADSORPTION LAYER AND THE ATTRACTIVE POTENTIALS

On the basis of molecular properties, Gregory (ref. 14) Tabor and Winterton (ref. 15) have related the Hamaker constant directly to the static dielectric constant. This value can be calculated both from Gregory's and Tabor and Winterton's expressions (ref. 15):

$$A = [(27/64) h\nu_k] (\epsilon_0 - 1 / \epsilon_0 + 2)^2 \quad (4)$$

where  $A$  is the Hamaker constant,  $h$  is the Planck constant,  $\nu_i$  is the characteristic dispersion frequency, determined by refractive index measurement in the visible region and  $\epsilon_0$  is the limiting dielectric constant ( $= n^2$ ). For calculating the van der Waals attraction between colloidal particles with adsorbed layers, extensions of the Vold approach have been made by Vincent et al (refs. 2,3). In the general case of two spherical particles the attraction energy is given by

$$V_A = -1/12 [H_{ls}(A_{ls}^{1/2} - A_m^{1/2})^2 + H_p(A_p^{1/2} - A_{ls}^{1/2})^2 + 2H_{pls}(A_p^{1/2} - A_{ls}^{1/2})(A_{ls}^{1/2} - A_m^{1/2})] \quad (5)$$

where the functions  $H(x,y)$  are expressed in ref. 3.

In the above equation,  $V_A$  is the attractive potential and  $A_m$ ,  $A_{ls}$ ,  $A_p$  are the Hamaker constants of the medium (bulk phase), the adsorbed layers and the spherical particles, respectively.

### RHEOLOGICAL PROPERTIES OF SUSPENSIONS

The rheological properties of dispersed systems are determined by particle-particle and particle-medium interactions. For plastic and pseudoplastic systems, the separation energy characteristic to particle-particle interactions can be calculated from the Bingham yield stress  $\tau_B$ . As it was reported in detail earlier (ref. 1), according to the principles R.J. Hunter, P.C. Neville, and B.A. Firth (refs. 16-18) separation energy can be given as follows:

$$E_{sep} = (\pi^2 r^3 / 3 \phi^2) \tau_B \quad (6)$$

where  $r$  is the radius and  $\phi$  is the volume fraction of the particles, respectively.

### RESULTS AND DISCUSSION

The behaviour of benzene(1)+n-heptane(2) and methanol(1)+benzene(2) mixtures adsorbed on hydrophobic Degussa aerosil R-972 were examined. Fig. 1 represents the comparison of the excess free energy, the enthalpy of wetting and the change of the Bingham yield stress. Fig. 1a shows the excess free energy change  $\Delta_2 G$  during adsorption with the molar fraction  $x_1$ . Calculations of  $\Delta_2 G$  were done on the basis of Eq. (1). The course of the function  $\Delta_2 G$  vs.  $x_1$  obtained for hydrophobic aerosil particles dispersed in benzene(1)+n-heptane(2) mixture uniquely indicates that adsorption of benzene in the surface layer results in the decrease of free energy. Fig. 1b illustrates the enthalpy of wetting  $\Delta_w H$  as a function of the molar fraction  $x_1$ . According to Fig. 1b, in all of the calorimetric investigations exothermic effects were observed. Thus it was established that the wetting of a hydrophobic silica particle is more pronounced in benzene than in n-heptane.

In accordance with the adsorption and immersion data, the Bingham yield stress obtained from flow curves is higher in n-heptane than in benzene, and the decrease was parallel to the improvement of wetting (Fig. 1c).

In methanol+benzene mixtures on hydrophobised aerosil surface, the  $\Delta_2 G$  curve of the free energy change reaches an extreme value at the adsorption azeotropic composition. The enthalpy of wetting function also has a nearly constant part at the azeotropic composition  $\phi_1^a$ . The slope of the curve indicates that the formation of the adsorption layer must be an important exothermic process throughout (Figs. 1d,e).

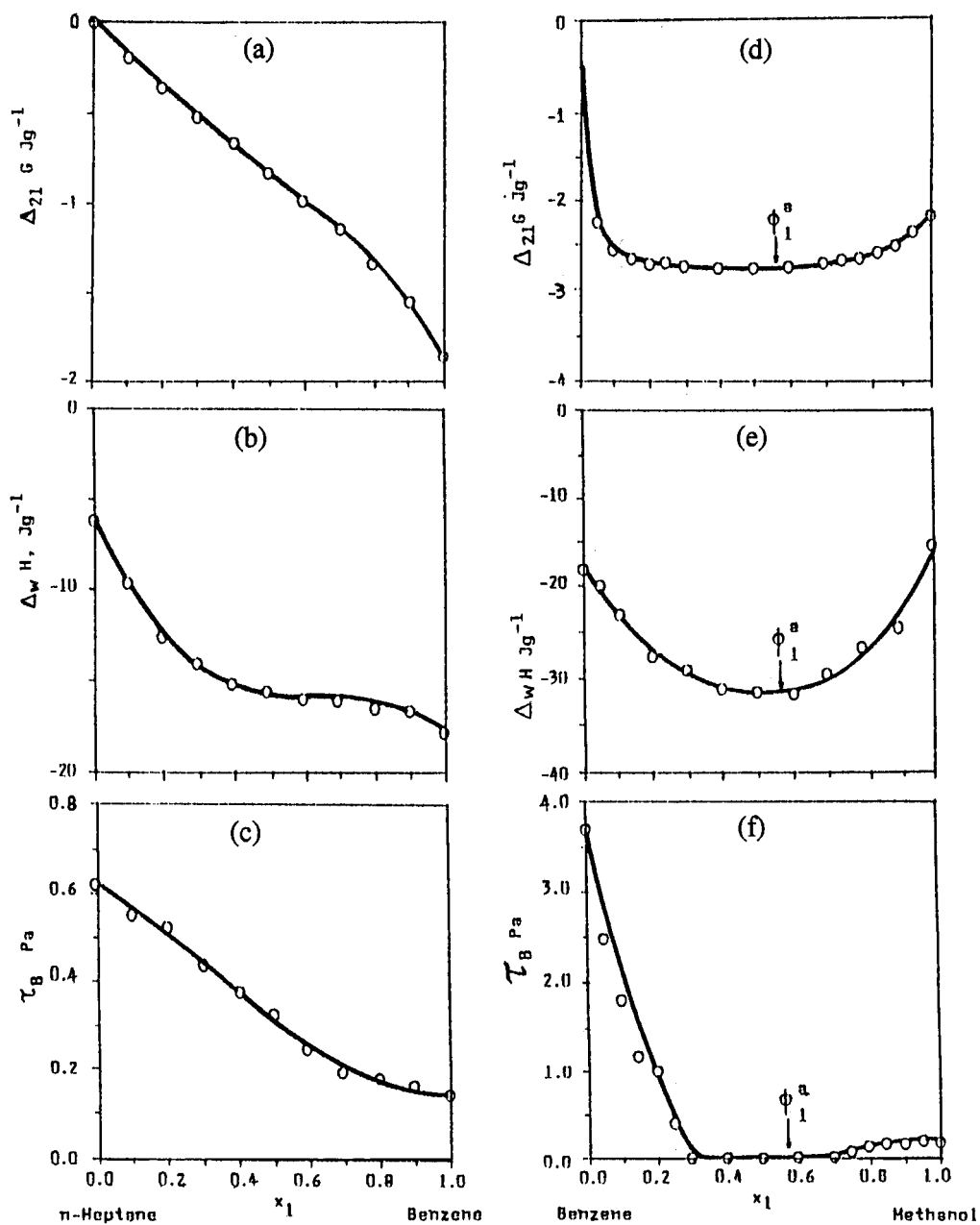


Fig. 1. Free energy  $\Delta_{21}G$ , enthalpy of wetting  $\Delta_w H$  and yield stress  $\tau_B$  on hydrophobic aerosil in liquid mixtures.

The function of the Bingham yield stress characteristic to the interparticle interaction disappears at the azeotropic mixture composition (Fig. 1f). (Flow curves obtained at various mixture compositions have been reported previously (ref. 1)). Thus, it is established that by decreasing the values of  $\Delta_{21}G$  and  $\Delta_w H$  the Bingham yield stress decreases dramatically until a Newtonian type flow azeotropic mixture composition of good stability is reached. The same tendency was observed for the values of the free energy, the enthalpy of wetting and the Bingham yield stress in suspensions, starting from methanol towards the azeotropic composition. This suggests that reaching the minimum of the free energy and the wetting enthalpy function guarantees minimal particle-particle interaction.

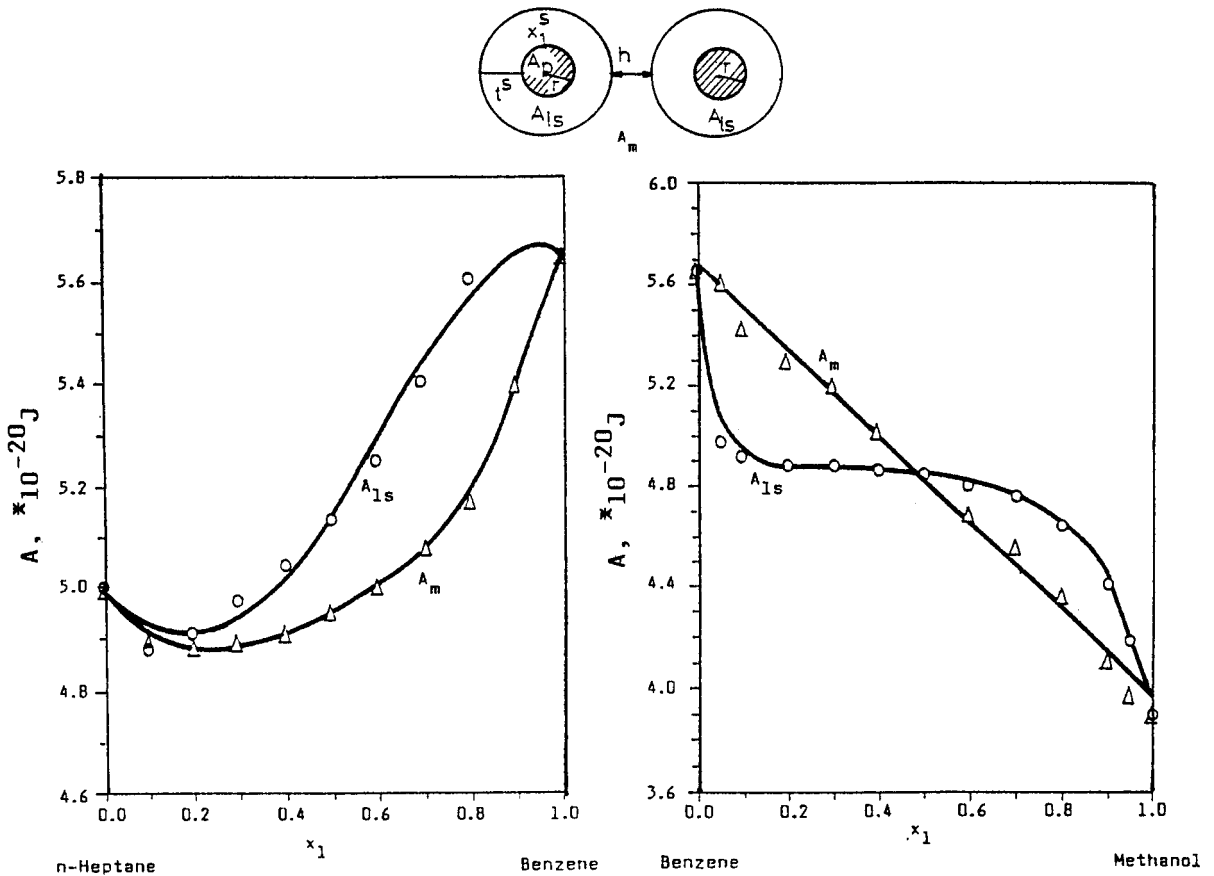


Fig. 2. The calculated Hamaker constants in bulk liquids ( $A_m$ ) and in the adsorption layer ( $A_{1s}$ ) in benzene+n-heptane and methanol+benzene mixtures.

On the basis of optical dispersion experiments the Hamaker constants of benzene+n-heptane and methanol+benzene mixture series were determined by Eq. (4) in Fig. 2. If the Hamaker constant of the adsorption layer of hydrophobic silica (R 972) is also reported with that of the bulk phase, the former changes in the same way (S-shaped) as in methanol+benzene, U-shaped in benzene+n-heptane.

The attractive potential for a given distance, calculated on the basis of the Vincent model was compared with the particle-particle separation energy in Fig. 3a,b. The attractive potential was found to decrease monotonously as a function of the mole fraction of the mixture series for benzene, just like the separation energy determined from the Bingham yield value. According to Fig. 3b, taking the adsorption layer into account, the separation values were lower than without that.

When calculations were effected for adsorption layers nearly in contact with one another, the attractive potential change via the mole fraction of methanol is illustrated on Fig. 3c. Comparison with the separation energy calculated from the Bingham yield stress in Fig. 3d emphasizes again the exceptional part of the adsorption azeotropic point. Thus, the application of the Vincent model appears to be absolutely necessary. Also, the thickness of the adsorption layer is of great importance. The application of the above model enables us to obtain correct results reflecting the relations between the separation energy, the excess free energy, the enthalpy of wetting and the attractive potential.

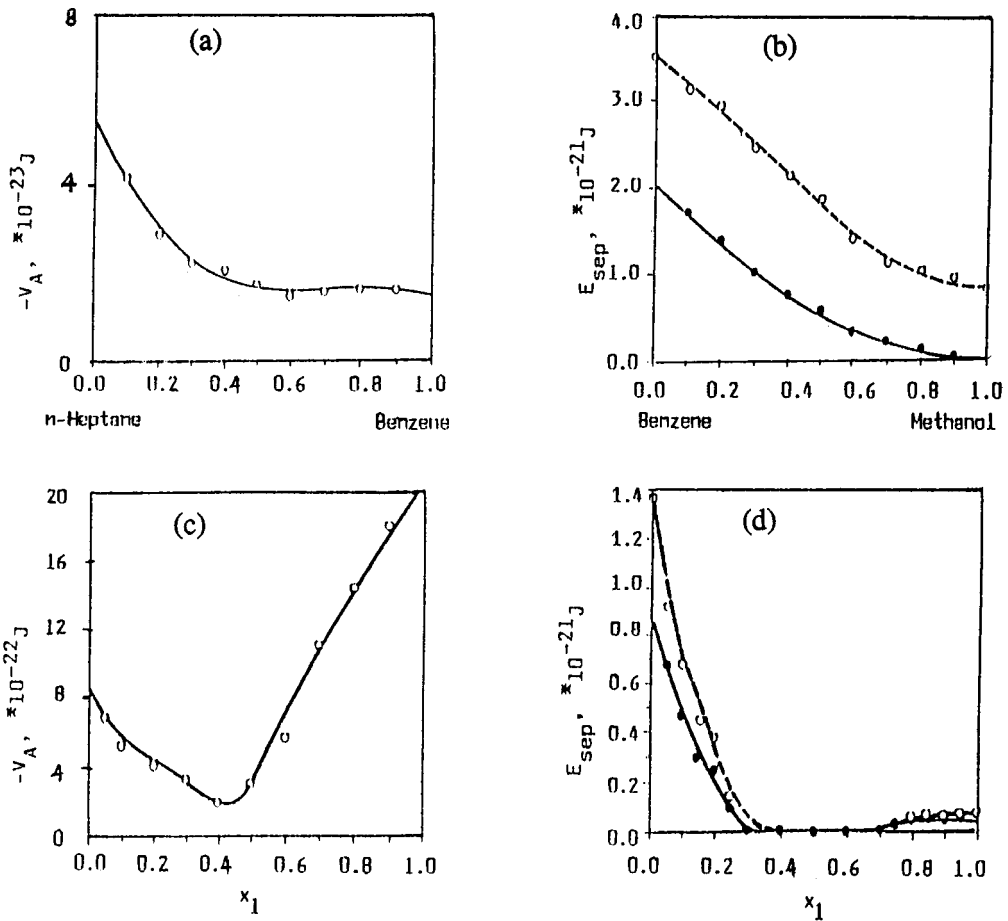


Fig. 3. The attraction energies and the separation energies in aerosol suspension of liquid mixtures.

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