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**Solvent dependent interactions between droplets in
water-in-oil microemulsions**

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Abstract:

In this paper, we investigated the dilution enthalpies of the droplets in water/AOT/oil microemulsions with the oil being isooctane, decane, cyclohexane by isothermal titration microcalorimetry (ITC). Combining with the results obtained from the study of water/AOT/toluene system in our previous work, it was found that the enthalpy interactions between droplets for isooctane and decane systems were repulsive, while the enthalpy interactions were attractive for cyclohexane and toluene systems. The repulsive droplet interaction for isooctane system was also confirmed by the static light scattering. The solvents appear to play important roles in varying the droplet enthalpy interactions from the positive to the negative, and the entropy contribution seems to be dominant for the stability of these microemulsion droplet systems.

Keywords: microemulsion droplet, interaction enthalpy, solvent effect, ITC, light scattering

1. Introduction

Water-in-oil microemulsions are transparent, isotropic and thermodynamically stable systems composed of a dispersion of water in oil stabilized by one or more other components (surfactant and cosurfactant) which are partially soluble in both water and oil. Microemulsions are of great interest in enhanced oil recovery, drug carriers, cosmetic materials, and microreactors etc.¹⁻³

The interactions between microemulsion droplets are closely associated with various applications of microemulsions. Despite the vast amount of work dealing with microemulsion properties including the interactions between the microemulsion droplets, the question of the origin of the interactions remains open. The overlapping effect between two microemulsion droplets and its contribution to the droplet energy potential were investigated early by Agterof et al. through light scattering experiments.⁴ Huang et al.^{5,6} and Pincus⁷ proposed a simple square-well model and suggested that the short range attractive interaction should be resulted from the overlapping between two microemulsion droplets and its strength increases with the droplet size. This assumption of the attractive interaction was thought to be confirmed by the neutron or light scattering measurements,^{6,8} particularly for the AOT/water/*n*-alkane microemulsions. However, the possible non-negative interaction enthalpies have been detected,^{9,10} which were unable to be interpreted by the square-well energy potential model. It was pointed that this attractive interaction potential should have a free-energy character.¹¹ Thermodynamic studies showed that drawing two droplets together and further forming the droplet cluster in the

AOT-based w/o microemulsions are possibly driven by the positive entropy change arising due to the release of solvent molecules that remain confined within the surfactant tails of the droplets.^{12,13} The increasing clustering in microemulsions as the temperature increases was also observed and interpreted by a repulsive sticky hard-sphere model in terms of a positive binding enthalpy by Koper.¹⁴ Lemaire et al.¹⁵ calculated the mean field intermicellar free energy potential including the contributions of enthalpy and entropy. Nagao et al. found a complicated picture of the concentration dependent interactions between microemulsion droplets and pointed that the complexities of the interaction among droplets could be the essential features of the colloidal systems and be one of future problems.¹⁶

The influences of the solvent nature on the extent of self-assembly and the nature of surfactant aggregate are fundamental questions, which reflects the solvent dependent interactions in the microemulsions.¹⁷ Wipf et al. pointed that the percolation transition is dependent on the droplet interaction which is mainly determined by the oil phase.¹⁸ Lemaire et al.¹⁵ suggested that the strength of the droplet attraction should be related to the ability of the continuous phase to penetrate into the aliphatic surfactant layer. Valeroa et al. confirmed that the longer chain length of oil had more difficulty in penetrating into the surface layer.¹⁹ Huang investigated the solvent dependence attractive interactions between microemulsion droplets for several *n*-alkanes with different chain lengths, and found that attractive strength generally increased with the chain length.⁶ The results of computed simulation obtained by Chan et al.²⁰ indicated that the short-range interactions between two surfaces of the droplets can be mediated

by a solvent, depending on the solvent parameters, the interaction can be repulsive or attractive. Recently, Salabat et al.²¹ used dynamic light scattering to monitor the apparent diffusion coefficient and effective microemulsion droplet diameter, and found that the interdroplet attractive interactions could be tuned by formulation of appropriate solvent mixtures using heptane, toluene, and dodecane. Myakonkaya et al.²² and Agazzi et al.²³ also found that the properties of the microemulsions and possibly also the droplet interaction can be controlled by changing the solvent blend composition. However, up to now, no direct experimental evidences involving the solvent dependent enthalpy interactions between the microemulsion droplets have been reported to clarify the existence of some ambiguities and contradictories. Therefore, direct measurements of the interaction enthalpies for the droplets in microemulsions composed of the same surfactant but different solvents to enhance the understanding of the influence of the solvent are highly required.

Microcalorimetry is the most direct tool in determining the interaction enthalpies between the microemulsion droplets. In our previous work, a new experiment process was designed to measure the real heat of dilution of the microemulsion droplets by isothermal titration microcalorimetry (ITC), and the negative interaction enthalpy of the droplets for water/sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/toluene system was obtained.²⁴ In this paper, we use ITC to determine the interaction enthalpies of water/AOT/oil microemulsion droplets with oil being isooctane, or decane, or cyclohexane. The ITC results are further confirmed by measurements of static light scattering at various temperatures. It has interestingly been found that the interaction

enthalpies for above microemulsions have different signs (positive or negative) for different solvents.

2. Experimental section

2.1. Materials. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) ($\geq 99\%$ mass fraction) was purchased from Sigma-Aldrich, and dried by P_2O_5 in a desiccator for two weeks before use. Cyclohexane ($\geq 99\%$ mass fraction) was obtained from Tianjin Chemical Reagent Company. Decane ($\geq 98\%$ mass fraction) and isooctane ($\geq 99\%$ mass fraction) were obtained from Tianjin Guangfu Chemical Reagent. Twice distilled water was used in preparations of the microemulsions throughout all experiments.

2.2. Microemulsion preparation. The microemulsions with required molar ratios ω of water to AOT were prepared by mixing proper amounts of water, AOT and isooctane or decane or cyclohexane and stirred until the solutions became transparent. The prepared microemulsions were set in a water bath with appropriate temperatures for 1 day for equilibriums before measurements. The concentrations of the prepared microemulsions were determined by weighing.

2.3. Isothermal titration microcalorimetry (ITC). The ITC experiment was conducted at 298.15 K using the Thermal Activity Monitor (Thermometric AB, Sweden). The detailed experiment process was reported in the previous work.²⁴ For preventing from the dissociation of the microemulsion droplets injected into the ampoule and the corresponding heat effect, a dilute microemulsion with the concentration and the mole quantity of the droplet being ρ_{20} and n_{20} , respectively, was loaded into the ampoule before the injection; here ρ is the number of droplets per nm^3 .

We used a Hamilton syringe to continuously inject a concentrated microemulsion with the concentration of the droplet being ρ_{2s} into the ampoule. The injection speed of the syringe and the stirring speed in the ampoule were $0.5 \mu\text{L}\cdot\text{s}^{-1}$ and 60 rpm, respectively. The enthalpy of mixing for each injection was determined. The relationship between the sum of the mixing enthalpy ΔH of i injections and the surfactant concentration ρ_{2i} of the droplets in the ampoule after the i th injection can be described by eqn (1) and (2)²⁴

$$\Delta H / \sum n_{2i} = \Delta H_2(\rho_{2s}) - \Delta H_p [(\sum n_{2i} + n_{20})\rho_{2i} / \sum n_{2i} - n_{20}\rho_{20} / \sum n_{2i}] \quad (1)$$

$$\Delta H_p = RT^2 dB/dT \quad (2)$$

where ΔH_p is the dilution enthalpy per mole microemulsion droplet for diluting a microemulsion with a fixed value of ω from the concentration being 1 droplet per nm^3 to the infinite; B is the second virial coefficient with the unit of nm^3 ; $\Delta H_2(\rho_{2s})$ is the molar dilution enthalpy of the droplet for diluting a microemulsion with the concentration of ρ_{2s} in the syringe to the infinite; $\sum n_{2i}$ is the total molar quantity of the droplet injected into the ampoule after the i th injection.

If a microemulsion droplet consists of N_{agg} AOT molecules and ωN_{agg} water molecules with N_{agg} being the aggregation number of AOT, eqn (1) and (2) may be rewritten as:

$$\Delta H / \sum n_{\text{suri}} = \Delta H_{\text{surs}}(C_{\text{surs}}) - \Delta H_{\text{Csur}} [(\sum n_{\text{suri}} + n_{\text{sur0}})C_{\text{suri}} / \sum n_{\text{suri}} - n_{\text{sur0}}C_{\text{sur0}} / \sum n_{\text{suri}}] \quad (3)$$

$$\Delta H_{\text{Csur}} = RT^2 N_A (dB/dT) / N_{\text{agg}}^2 = \Delta H_p N_A / N_{\text{agg}}^2 \quad (4)$$

where ΔH_{Csur} is the dilution enthalpy per mole surfactant for diluting a microemulsion with a fixed value of ω from the surfactant concentration being $1 \text{ mol}\cdot\text{cm}^{-3}$ to the

infinite; N_A is the Avogadro's constant; $C_{\text{sur}0}$ and $C_{\text{sur}i}$ are the concentrations of the surfactant in the ampoule with the unit of $\text{mol}\cdot\text{cm}^{-3}$ before the injection starts and after the i th injection, respectively; $n_{\text{sur}0}$ and $\sum n_{\text{sur}i}$ are the molar quantities of the surfactant in the ampoule before the injection and after the i th injection, respectively.

If a microemulsion droplet has a volume v_{droplet} with the unit of nm^3 , eqn (1) may be rewritten as

$$\Delta H / \sum n_{2i} = \Delta H_2(\rho_{2s}) - \Delta H_p [(\sum n_{2i} + n_{20})\rho_{2i}v_{\text{droplet}} / \sum n_{2i} - n_{20}\rho_{20}v_{\text{droplet}} / \sum n_{2i}] / v_{\text{droplet}} \quad (5)$$

where $\rho_{20}v_{\text{droplet}} = \phi_{20}$ and $\rho_{2i}v_{\text{droplet}} = \phi_{2i}$ with ϕ_{20} and ϕ_{2i} being the droplet volume fractions in the ampoule before the injection and after the i th injection, respectively, thus eqn (5) becomes

$$\Delta H / \sum n_{2i} = \Delta H_2(\rho_{2s}) - \Delta H_\phi [(\sum n_{2i} + n_{20})\phi_{2i} / \sum n_{2i} - n_{20}\phi_{20} / \sum n_{2i}] \quad (6)$$

$$\Delta H_\phi = \Delta H_p / v_{\text{droplet}} \quad (7)$$

where ΔH_ϕ is the molar enthalpy of the droplets with a fixed value of ω for hypothetically diluting pure droplets into the infinite dilution.

The relative uncertainties in determinations of ΔH , ΔH_{Csur} , ΔH_p and ΔH_ϕ were estimated to be less than 15 % of the values.

2.4. Static light scattering. A Brookhaven BI200SM goniometer and BI9000 digital correlator were used to perform the static light scattering measurements. The measurement angle was fixed at 90° . The light source is an argon-ion laser with a wavelength of 488 nm. Solutions were filtered with Millipore 0.22 μm filters before measurements to remove the dust.

A series of Rayleigh ratios R at various surfactant concentrations C with the unit of

$\text{g}\cdot\text{cm}^{-3}$ were measured and the weight-averaged molar mass M of the droplet and the second virial coefficient B_2 with the unit of $\text{mol}\cdot\text{cm}^3\cdot\text{g}^{-2}$ were deduced from eqn (8)^{25,26}

$$KC/R = 1/M + 2B_2C \quad (8)$$

where $K = 4\pi^2 n^2 (\text{dn}/\text{d}C)^2 / (N_A \lambda^4)$ with n , $\text{dn}/\text{d}C$ and λ being the solvent refractive index, the differential refractive index increment, and the wavelength of the incident light in vacuo, respectively. The value of $\text{dn}/\text{d}C$ was determined by a differential refractometer (BI-DNDC, Brookhaven Instruments Corporation). The value of B_2 can be converted to the second virial coefficient B with the unit of nm^3 by eqn (9)^{26,27}

$$B = (B_2 M^2 / N_A) \times 10^{21} \quad (9)$$

3. Results and discussion

3.1. Water/AOT/Isooctane System

The water/AOT/isooctane microemulsions with ω being fixed at 15 and 40 and the concentrations of AOT (C_{AOT}) being $0.4 \text{ mol}\cdot\text{dm}^{-3}$, $0.02 \text{ mol}\cdot\text{dm}^{-3}$ and $0.016 \text{ mol}\cdot\text{dm}^{-3}$ were prepared. The titrations of the concentrated microemulsion ($C_{\text{AOT}} = 0.4 \text{ mol}\cdot\text{dm}^{-3}$) into the dilution ones ($C_{\text{AOT}} = 0.02 \text{ mol}\cdot\text{dm}^{-3}$ for $\omega = 15$ and $C_{\text{AOT}} = 0.016 \text{ mol}\cdot\text{dm}^{-3}$ for $\omega = 40$) were carried out to obtain the sums of the mixing enthalpies ΔH for i injections. According to eqn (3), plots of $\Delta H / \sum n_{\text{suri}}$ versus $\beta_c = [(\sum n_{\text{suri}} + n_{\text{sur0}})C_{\text{suri}} / \sum n_{\text{suri}} - n_{\text{sur0}}C_{\text{sur0}} / \sum n_{\text{suri}}]$ give straight lines as shown in Figs. 1a and 1b for microemulsions with ω being 15 and 40, respectively. We obtained the values of ΔH_{Csur} by linear least-squares fits, which together with the values of the correlation coefficient (r^2) are listed in lines 2 and 3 of Table 1.

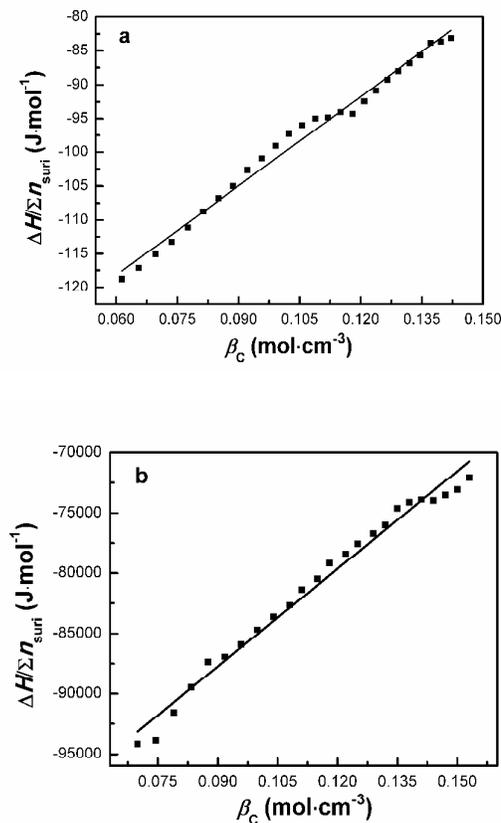


Fig. 1 Plots of $\Delta H/\Sigma n_{\text{suri}}$ versus $\beta_c = [(\Sigma n_{\text{suri}} + n_{\text{sur0}})C_{\text{suri}}/\Sigma n_{\text{suri}} - n_{\text{sur0}}C_{\text{sur0}}/\Sigma n_{\text{suri}}]$ for water/AOT/isooctane microemulsions. (a) Titrating the concentrated microemulsion ($C_{\text{AOT}} = 0.4 \text{ mol}\cdot\text{dm}^{-3}$) into the dilution one ($C_{\text{AOT}} = 0.02 \text{ mol}\cdot\text{dm}^{-3}$) for $\omega=15$; (b) Titrating concentrated microemulsion ($C_{\text{AOT}} = 0.4 \text{ mol}\cdot\text{dm}^{-3}$) into the dilution one ($C_{\text{AOT}} = 0.016 \text{ mol}\cdot\text{dm}^{-3}$) for $\omega=40$. The points represent the experimental results and the lines represent the results of the least-squares fittings.

Table 1 Aggregation numbers N_{agg} ; interaction enthalpies $-\Delta H_{\text{Csur}}$, $-\Delta H_{\text{p}}$, $-\Delta H_{\text{f}}$; correlation coefficients r^2 of fitting eqn. (3) and derivatives of the second virial coefficient with respect to the temperature dB/dT for water/AOT/oil

microemulsions at 298.15K

oil	ω	N_{agg}	$-\Delta H_{\text{Csur}}$ (J·dm ³ ·mol ⁻²)	r^2	$-\Delta H_{\text{p}}$ (J·nm ³ ·mol ⁻¹)	dB/dT (nm ³ ·K ⁻¹)	$-\Delta H_{\text{f}}$ (kJ·mol ⁻¹)
isooctane	15	212 ^a	441±64	0.985	(3.3±0.4)×10 ⁷	-46±5	141±20
isooctane	40	984 ^b	299±41	0.983	(4.9±0.7)×10 ⁸	-651±98	269±40
decane	15	228 ^a	378±56	0.997	(3.3±0.5)×10 ⁷	-44±6	130±19
cyclohexane	15	178 ^c	-172±24	0.964	(-9.1±1.0)×10 ⁶	12.3±0.2	-42±7
toluene	12	90 ^d	-307±43	0.996	(-4.1±0.6)×10 ⁶	5.6±0.8	-45±7

^a Determined by Amararene et.al.²⁸

^b Determined by static light scattering in this work.

^c Reported by Maitra.²⁹

^d Determine by static light scattering in our previous work.²⁶

The values of the dilution enthalpies ΔH_{Csur} were negative, indicating that pulling away two microemulsions droplets in water/AOT/isooctane microemulsions decreases the enthalpies of the systems and thus the interaction enthalpies $-\Delta H_{\text{Csur}}$ between the droplets are positive, which are consistent with that deduced from the small angle x-ray scattering data and the dielectric measurements for the water/AOT/isooctane microemulsion systems,¹⁴ however opposite to what we observed in the

water/AOT/toluene system,²⁴ which are listed the line 6 of Table 1 for comparison. It is the direct evidence from measurement of the heat of dilution that confirms the existence of the solvent dependent repulsive enthalpy interaction between the microemulsion droplets, and is unable to be interpreted by the attractive square-well energy potential model.

Robertus et al.³⁰ studied the clustering process in the water/AOT/isooctane microemulsion by dielectric relaxation spectroscopy and small-angle x-ray scattering and observed a strong interaction between the droplet and the solvent medium. Smeets et al.³¹ measured the viscosity of the water/AOT/isooctane microemulsion as a function of the droplet volume fraction at different temperatures, they found that the droplets behaved as suspension of sticky hard spheres, and the solvent molecules entrapped between the surfactant tails. Alexandridis et al.¹² showed that the transfer of water/AOT/isooctane microemulsion droplets from solution to the percolating cluster was an enthalpically-disfavored endothermic process. These experimental results were in consistent with our results, which supported the following explanation of the apparent repulsive enthalpy between the droplets. When two droplets close each others, the overlapping between droplets is accompanied by release of the solvent molecules.¹⁵ The interaction enthalpy difference between the interpenetration of the surfactant tails of two neighboring droplets and entrapping the solvent medium molecules into the surfactant tails decides the sign of ΔH_{Csur} , which is dependent on the nature of the solvent molecules and the microemulsion droplets. In the water/AOT/isooctane microemulsion, the isooctane molecules were more preferred in

the enthalpy to be entrapped in the surfactant tails than the interpenetration of two neighboring droplets, thus negative $\Delta H_{C_{sur}}$ was observed; while the toluene molecules were less enthalpically preferred to be entrapped in the surfactant tails than the interpenetration of two neighboring droplets in the water/AOT/toluene system, resulting a positive $\Delta H_{C_{sur}}$.

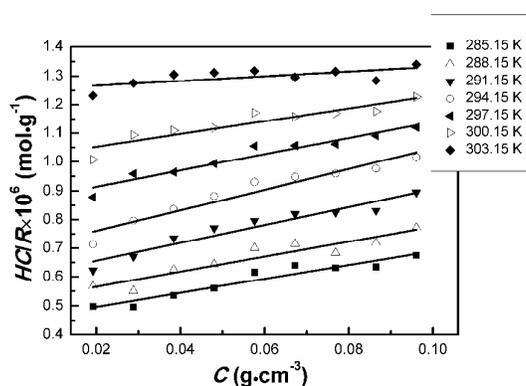


Fig. 2 Plots of KC/R versus C at different temperatures for water/AOT/isooctane microemulsion with $\omega=40$. The points represent the experimental results and the lines represent the results of least-squares fittings.

In order to confirm the ITC results, we carried static light scattering measurements at a fixed angle of 90° for a series of surfactant concentrations C in the water/AOT/isooctane microemulsion with ω being 40 at various temperatures. According to eqn (8), plots of KC/R versus C for different temperatures yield straight lines as shown in Fig. 2. The values of weight-averaged molar mass M of the droplet and the second virial coefficient B_2 were obtained by least-squares fits of eqn (8), and the values of B_2 were used to calculate the second virial coefficient B through eqn (9).

The values of M and B are listed in columns 2 and 3 of Table 2. The aggregation numbers N_{agg} were then calculated by:

$$N_{\text{agg}} = M/(\omega M_w + M_s) \quad (10)$$

which are listed in column 4 of Table 2. Analysis of the values of N_{agg} at different temperatures showed linear dependences of N_{agg} on the temperature. Interpolation of this linear relation gave the values of N_{agg} at 298.15 K, which was 984 ± 20 (see Table 1) and consist with the literature value of 965.²⁹ The values of the second virial coefficient B are all positive, and decrease linearly with the temperature as shown in Fig. 3, which agrees with that reported in literatures,^{14,16,21,32} but opposite to what observed in the water/AOT/toluene system.²⁶ It indicates that the enthalpy interaction between the water/AOT/isooctane droplets is repulsive. The value of dB/dT was obtained by a least-square fit of the linear relation between B and T , which was $-545 \pm 34 \text{ nm}^3 \cdot \text{K}^{-1}$, agrees with the values of dB/dT ($-651 \pm 98 \text{ nm}^3 \cdot \text{K}^{-1}$, see Table 1) calculated by eqn (4) using the aggregation numbers N_{agg} and the ITC results. Substituting the value of dB/dT and N_{agg} into eqn (4), we obtained the values of $-\Delta H_{\text{Csur}}$, and $-\Delta H_{\rho}$ which were $250 \pm 25 \text{ J} \cdot \text{dm}^3 \cdot \text{mol}^{-2}$ and $(4.1 \pm 0.4) \times 10^8 \text{ J} \cdot \text{nm}^3 \cdot \text{mol}^{-1}$, respectively. They are in reasonably good agreement with the values of $299 \pm 41 \text{ J} \cdot \text{dm}^3 \cdot \text{mol}^{-2}$ and $(4.9 \pm 0.7) \times 10^8 \text{ J} \cdot \text{nm}^3 \cdot \text{mol}^{-1}$ from ITC.

It is well known that more generally, instead of the attractive square-well energy potential model, the second virial coefficient should be expressed as the sum of the contributions of enthalpy and entropy^{15,33,34}

$$B = -\Delta H_{\rho}/(RT) + \Delta S_{\rho}/R \quad (11)$$

where $-\Delta S_p$ is the interaction entropy per mole droplet. As shown in Fig. 3, a plot of B versus the reciprocal of temperature also yields a straight line, indicating that ΔH_p and ΔS_p in eqn (11) are almost temperature independent in the temperature range we investigated. A least-squares fit of eqn (11) gave the values of $-\Delta H_p$ and $-\Delta S_p$ being $(3.9\pm 0.3)\times 10^8 \text{ J}\cdot\text{nm}^3\cdot\text{mol}^{-1}$ and $(1.3\pm 0.1)\times 10^6 \text{ J}\cdot\text{nm}^3\cdot(\text{mol}\cdot\text{K})^{-1}$, respectively; the former was reasonably well accorded with $(4.9\pm 0.7)\times 10^8 \text{ J}\cdot\text{nm}^3\cdot\text{mol}^{-1}$ determined by ITC. The positive interaction entropy may be interpreted by that when two droplets close together the isooctane molecules entrapped in the surfactant tails are released into the bulk solution and increase the entropy of the system, which suggests that the aggregation of the water/AOT/isooctane droplets may be driven by the entropy contribution.

Table 2 Microscopic parameters of water/AOT/ isooctane microemulsion with $\omega=40$ determined by static light scattering at various temperatures.

T (K)	M ($\text{g}\cdot\text{mol}^{-1}$)	B (nm^3)	N_{agg}
285.15	$(2.23\pm 0.09)\times 10^6$	9980 ± 28	1916 ± 73
288.15	$(1.95\pm 0.09)\times 10^6$	8297 ± 27	1674 ± 74
291.15	$(1.68\pm 0.06)\times 10^6$	7382 ± 23	1447 ± 51
294.15	$(1.45\pm 0.05)\times 10^6$	6228 ± 20	1245 ± 41
297.15	$(1.17\pm 0.02)\times 10^6$	3173 ± 12	1001 ± 21
300.15	$(9.92\pm 0.02)\times 10^5$	1834 ± 9	852 ± 18
303.15	$(7.99\pm 0.01)\times 10^5$	429 ± 4	686 ± 11

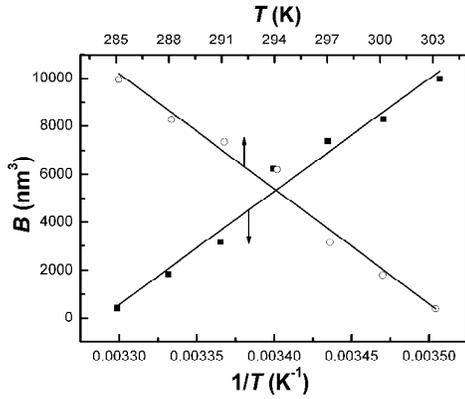


Fig. 3 Plots of B versus T or $1/T$ for water/AOT/isooctane microemulsion with $\omega=40$. The points represent the experimental results and the lines represent the results of least-squares fittings.

The values of $-\Delta H_p$ and dB/dT for water/AOT/isooctane microemulsion with $\omega=15$ were obtained through eqn (4) by using the value of aggregation number taken from the literature.²⁸ The calculated results are also listed in line 1 of Table 1.

With an assumption that the excess volumes may be neglected for mixing AOT, water and the solvent isooctane to form the microemulsion, thus the volume fractions ϕ_{20} and ϕ_{2i} may be calculated by

$$\phi_{20} = \frac{C_{\text{sur0}} M_{\text{AOT}}}{d_{\text{AOT}}} + \frac{C_{\text{sur0}} \omega M_{\text{H}_2\text{O}}}{d_{\text{H}_2\text{O}}} \quad (12)$$

$$\phi_{2i} = \frac{C_{\text{suri}} M_{\text{AOT}}}{d_{\text{AOT}}} + \frac{C_{\text{suri}} \omega M_{\text{H}_2\text{O}}}{d_{\text{H}_2\text{O}}} \quad (13)$$

where d_{AOT} and $d_{\text{H}_2\text{O}}$ are the densities of AOT and water with the units being $\text{g}\cdot\text{cm}^{-3}$.

A plot of $\Delta H/\sum n_{2i}$ versus $[(\sum n_{2i} + n_{20})\phi_{2i}/\sum n_{2i} - n_{20}\phi_{20}/\sum n_{2i}]$ gives a straight line as shown in Fig. 4. The values of ΔH , ϕ_{20} , ϕ_{2i} , n_{2i} and n_{20} were used to fit eqn (6) to obtain $-\Delta H_p$, which were $141\pm 20 \text{ kJ}\cdot\text{mol}^{-1}$ and $269\pm 40 \text{ kJ}\cdot\text{mol}^{-1}$ for

water/AOT/isooctane microemulsions with $\omega=15$ and $\omega=40$ (see column 8 of Table 1), respectively. The values of correlation coefficient of fitting eqn (6) were found to be almost the same as that of fitting eqn (3) for water/AOT/isooctane microemulsions and also for those with different solvents discussed in latter sections. The repulsive enthalpy interactions between the droplets in the above two microemulsion systems increased with the molar ratio of water to AOT, which well accorded with what observed by Dijk³⁵ and Smeets.³¹ They experimentally found $-\Delta H_\phi=119 \text{ kJ}\cdot\text{mol}^{-1}$ for $\omega=35$ and $-\Delta H_\phi=75 \text{ kJ}\cdot\text{mol}^{-1}$ for $\omega=25$, and $-\Delta H_\phi=121 \text{ kJ}\cdot\text{mol}^{-1}$ for $\omega=35$ and $-\Delta H_\phi=89 \text{ kJ}\cdot\text{mol}^{-1}$ for $\omega=25$, respectively. It may be interpreted by that the smaller microemulsion droplets have more ordered and rigid surfactant interface,¹⁸ which increases the enthalpy of entrapping the isooctane molecules into the surfactant tails.

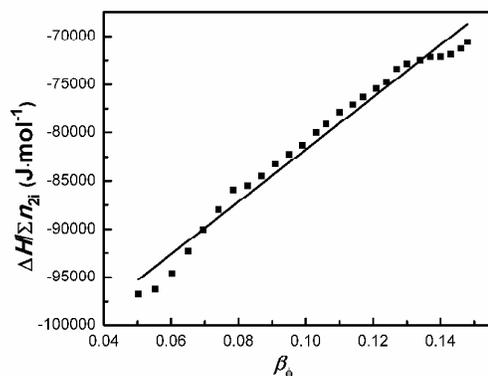


Fig. 4 Plot of $\Delta H/\sum n_{2i}$ versus $\beta_\phi = [(\sum n_{2i} + n_{20})\phi_{2i}/\sum n_{2i} - n_{20}\phi_{20}/\sum n_{2i}]$ for water/AOT/isooctane microemulsion with ω being 40.

3.2. Water/AOT/Decane System

The water/AOT/decane microemulsions with the value ω being fixed at 15 and the

concentrations of AOT being $0.5 \text{ mol}\cdot\text{dm}^{-3}$ and $0.025 \text{ mol}\cdot\text{dm}^{-3}$ were prepared. The continuous titrations of the concentrated microemulsion ($C_{\text{AOT}} = 0.5 \text{ mol}\cdot\text{dm}^{-3}$) into the dilution one ($C_{\text{AOT}} = 0.025 \text{ mol}\cdot\text{dm}^{-3}$) were carried out to obtain the sum of the mixing enthalpies ΔH of i injections. According to eqn (3), a plot of $\Delta H/\sum n_{\text{suri}}$ versus $\beta_\phi = [(\sum n_{2i} + n_{20})\phi_{2i}/\sum n_{2i} - n_{20}\phi_{20}/\sum n_{2i}]$ gives a straight line as shown in Fig. 5. We obtained the value of ΔH_{Csur} by a least-squares fit. The values of $-\Delta H_p$, dB/dT and $-\Delta H_\phi$ then were obtained through eqn (4) and (6) by using the value of aggregation number taken from the literature.²⁸ The calculated results together with the value of the correlation coefficient for fitting eqn (3) are listed in line 4 of Table 1.

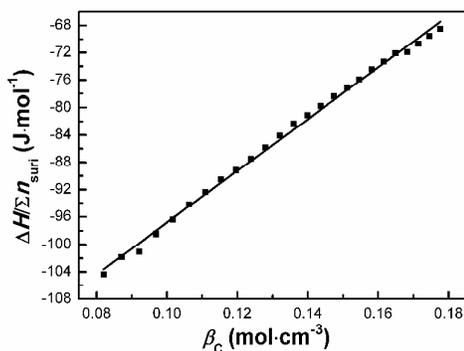


Fig. 5 A plot of $\Delta H/\sum n_{\text{suri}}$ versus $\beta_c = [(\sum n_{\text{suri}} + n_{\text{sur0}})C_{\text{suri}}/\sum n_{\text{suri}} - n_{\text{sur0}}C_{\text{sur0}}/\sum n_{\text{suri}}]$ for water/AOT/decane microemulsion with $\omega=15$. The points represent the experimental results and the line represents the result of the least-squares fitting.

Similar to water/AOT/isooctane but opposite to water/AOT/toluene, the values of ΔH_{Csur} , ΔH_p and ΔH_ϕ for water/AOT/decane microemulsion are negative, indicating a repulsive enthalpy interaction between the microemulsion droplets. These results are

contradictory to that reported in literatures for the same system,^{8,36} where the light or neutron scattering data together with the model potential of a hard core plus an attractive square well were used to calculate the attractive interaction energy. However the positive interaction enthalpies of droplets for water/AOT/decane microemulsion was supported by the percolating experimental results.¹²

The repulsive enthalpy interaction between the droplets for water/AOT/decane system suggests that the aggregation of the droplets which drive the phase separation of the system should be interpreted by the entropy effect. This mechanism could also explain the existence of the low critical temperature for this system:³⁷ increase of the temperature promotes the release of the solvent molecules into the bulk solution and increases the entropy of the system, which results in the aggregation of the droplets and further the phase separation.

3.3. Water/AOT/Cyclohexane System

The water/AOT/cyclohexane microemulsions with the value ω being fixed at 15 and the concentrations of AOT being $0.4 \text{ mol}\cdot\text{dm}^{-3}$ and $0.02 \text{ mol}\cdot\text{dm}^{-3}$ were prepared. The continuous titrations of the concentrated microemulsion ($C_{\text{AOT}} = 0.4 \text{ mol}\cdot\text{dm}^{-3}$) into the dilution one ($C_{\text{AOT}} = 0.02 \text{ mol}\cdot\text{dm}^{-3}$) were carried out to obtain ΔH . A plot of $\Delta H/\sum n_{\text{suri}}$ versus $\beta_{\phi} = [(\sum n_{2i} + n_{20})\phi_{2i}/\sum n_{2i} - n_{20}\phi_{20}/\sum n_{2i}]$ yields a straight line and is shown in Fig. 6. A least-squares fit gave $\Delta H_{\text{Csur}} = 172 \pm 24 \text{ J}\cdot\text{dm}^3\cdot\text{mol}^{-2}$ at 298.15 K. The values of $-\Delta H_p$, dB/dT and $-\Delta H_{\phi}$ at 298.15 K then were obtained through eqn (4) and (6) by using the value of aggregation number taken from the literature.²⁹ All the results together with the value of the correlation coefficient for fitting eqn (3) are

listed in line 5 of Table 1. The positive values of $\Delta H_{C_{sur}}$, ΔH_p and ΔH_ϕ suggest that the enthalpy interaction between the microemulsion droplets in water/AOT/cyclohexane microemulsion should be attractive, which is consistent with that observed in the water/AOT/toluene microemulsion.²⁴ The apparent attractive enthalpy interaction may be attributed to the enthalpically stronger overlapping of the tails of the surfactant^{15,16} and the weaker attractive enthalpy interaction of cyclohexane or toluene with the surfactant tails.

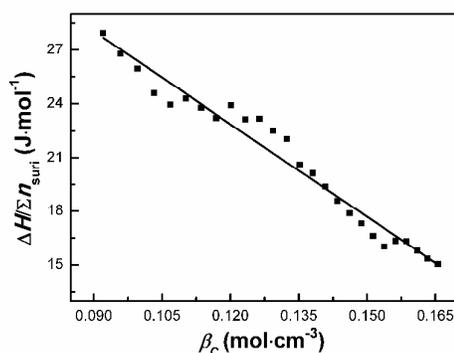


Fig. 6 A plot of $\Delta H/\Sigma n_{suri}$ versus $\beta_c = [(\Sigma n_{suri} + n_{sur0})C_{suri}/\Sigma n_{suri} - n_{sur0}C_{sur0}/\Sigma n_{suri}]$ for water/AOT/cyclohexane microemulsion with $\omega=15$. The points represent the experimental results and the line represents the result of the least-squares fitting.

3.4. Solvent Effect on the Interactions between the Microemulsion Droplets

The solvents used in the present study may be conveniently divided into two groups: the first group has sphere-like molecular structure, *viz.* toluene and cyclohexane; and the second group has cylinder-like molecular structure, *viz.* decane and isooctane. The cylinder-like decane and isooctane molecules possibly are more compatible with the AOT tails than the sphere-like toluene and cyclohexane molecules, thus they are

enthalpically more favorable to be entrapped in the surfactant tails than toluene and cyclohexane .

When two droplets close each other, the overlapping of the surfactant tails between the two neighboring droplets results in the release of the entrapped solvent molecules, thus the apparent interaction enthalpy between the microemulsion droplets depends on the competition of the enthalpy changes of overlapping of the surfactant tails between two neighboring droplets and the release of the entrapped solvent molecules. The positive apparent interaction enthalpies for water/AOT/isooctane and water/AOT/decane indicated that the enthalpies of entrapping these solvent molecules are lower than that of overlapping the surfactant tails of two neighboring droplets, but the contrary is the case in the toluene or cyclohexane system.

Some studies have suggested that the microemulsion system with toluene or cyclohexane being the solvent is more stable than that of isooctane or *n*-alkane and concluded that isooctane and *n*-alkane were more difficult to penetrate into the surfactant tails and thus resulted in stronger net attraction between two droplets than toluene and cyclohexane.^{13,21,22} This net attraction should have a free-energy character as pointed by Vrij.¹¹ Thus combining with our new observations of stronger attractive enthalpy interaction between droplets for water/AOT/toluene and water/AOT/cyclohexane systems, it may conclude that the higher stabilities of toluene and cyclohexane entrapped between the AOT tails and hence of their microemulsion systems as compared with water/AOT/isooctane and water/AOT/decane are resulted from the entropy contributions, i.e. entrapping toluene and cyclohexane molecules

between the AOT tails losses less entropy than that of isooctane and *n*-alkane molecules, or pulling two microemulsion droplets together produces less entropy for water/AOT/toluene and water/AOT/cyclohexane than for water/AOT/isooctane and water/AOT/decane.

Conclusion

The dilution enthalpies of microemulsions of water/AOT/isooctane, water/AOT/decane, and water/AOT/cyclohexane were measured by ITC to directly determine the enthalpies of the droplet interactions. Combining with the results of water/AOT/toluene system we studied previously, it was found that for isooctane and decane systems, the interaction enthalpies between droplets were positive, indicating the repulsive droplet interactions; while the interaction enthalpies were negative and the droplet interactions were attractive for cyclohexane and toluene systems. The repulsive droplet interaction for isooctane system with the molar ratio of water to AOT being 40 was also confirmed by static light scattering, which showed that the second virial coefficient of this system decreased with temperature. The apparent interaction enthalpy between the microemulsion droplets is believed to be decided by the competition of the enthalpy changes due to overlapping of the surfactant tails between two neighboring droplets and the release of the entrapped solvent molecules into the bulk solution, which depends on the compatibility of the solvent with the AOT tails. This enthalpy interaction effect on the stability of the microemulsion droplets we studied was found to be opposite to that characterized by the "free-energy

interaction" and extracted from some reported investigations, indicating an important entropy contribution, which required to be further confirmed. Therefore more extended calorimetric studies and light scattering investigations on characteristic enthalpy features of the droplet-droplet interactions including the aggregation numbers in reversed micelles and microemulsions, such as the effects of the solvent, droplet size and the chain length of the alkane solvents, are underway.

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References

- (1) Pileni, M. P. *J. Phys. Chem.* **1993**, *97*, 6961.
- (2) Moulik, S. P.; Rakshit, A. K. *J. Surf. Sci. Technol.* **2006**, *22*, 159.
- (3) Chen, Z. y.; Zhao, J. h.; He, W.; An, X. q.; Shen, W. g. *Int. J. Chem. Kinet.* **2008**, *40*, 294.
- (4) Agterof, W. G. M.; van Zomeren, J. A. J.; Vrij, A. *Chem. Phys. Lett.* **1976**, *43*, 363.
- (5) Huang, J. S.; Safran, S. A.; Kim, M. W.; Grest, G. S. *Phys. Rev. Lett.* **1984**, *53*, 592.
- (6) Huang, J. S. *J. Chem. Phys.* **1985**, *82*, 480.
- (7) Pincus, P. A. *J. Chem. Phys.* **1987**, *86*, 1644.
- (8) Dozier, W. D.; Kim, M. W.; Kleins, R. *J. Chem. Phys.* **1987**, *87*, 1455.
- (9) Goffredi, F.; Liveri, V. T.; Vassallo, G. *J. Colloid Interface Sci.* **1992**, *151*,

396.

(10)Fini, P.; Castagnolo, M.; Catucci, L.; Cosma, P.; Agostiano, A. *Colloids Surf., A* **2004**, *244*, 179.

(11)Vrij, A. *Pure & Appl Chem.* **1976**, *48*, 471—483.

(12)Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. *J. Phys. Chem.* **1995**, *99*, 8222.

(13)Cason, J. P.; Miller, M. E.; Thompson, J. B.; Roberts, C. B. *J. Phys. Chem. B* **2001**, *105*, 2297.

(14)Koper, G. J. M.; Bedeaux, D. *Physica A* **1992**, *187*, 489.

(15)Lemaire, B.; Bothorel, P.; Roux, D. *J. Phys. Chem.* **1983**, *87*, 1023.

(16)Nagao, M. *Physical Review E* **2007**, *75*, 061401(1).

(17)Hollamby, M. J.; Tabor, R.; Mutch, K. J.; Trickett, K.; Eastoe, J.; Heenan, R. K.; Grillo, I. *Langmuir* **2008**, *24*, 12235.

(18)Wipf, R.; Jaksch, S.; Stühn, B. *Colloid Polym. Sci.* **2010**, *288*, 589.

(19)Valeroa, M.; Sanchez, F.; Gomez-Herrera, C.; Lopez-Cornejo, P. *Chemical Physics* **2008**, *345*, 65.

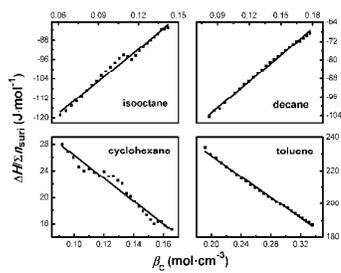
(20)Chan, D. Y. C.; Mitchell, D. J.; Ninham, B. W.; Pailthorpe, B. A. *Mol. Phys.* **1978**, *35*, 1669.

(21)Salabat, A.; Eastoe, J.; Mutch, K. J.; Tabor, R. F. *J. Colloid Interf. Sci.* **2008**, *318*, 244.

(22)Myakonkaya, O.; Eastoe, J.; Mutch, K. J.; Rogers, S.; Heenan, R.; Grillo, I. *Langmuir* **2009**, *25*, 2743.

- (23) Agazzi, F. M.; Falcone, R. D.; Silber, J. J.; Correa, N. M. *J. Phys. Chem. B* **2011**, *115*, 12076.
- (24) Zheng, P.; Ma, Y.; Peng, X.; Yin, T.; An, X.; Shen, W. *Langmuir* **2011**, *27*, 12280.
- (25) Zhou, S.; Wu, C. *Macromolecules* **1995**, *28*, 5225.
- (26) Peng, X. H.; Zheng, P. Z.; Ma, Y. M.; Yin, T. X.; An, X. Q.; Shen, W. G. *Acta Phys. Chim. Sin.* **2011**, *27*, 1026.
- (27) Li, P.; An, X. Q.; Shen, W. G. *Acta Phys. Chim. Sin.* **2001**, *17*, 144.
- (28) Amararene, A.; Gindre, M.; Huérou, J.-Y. L.; Urbach, W.; Valdez, D.; Waks, M. *Phys. Rev. E* **2000**, *60*, 682.
- (29) Maitra, A. *J. Phys. Chem.* **1984**, *88*, 5122.
- (30) Robertus, C.; Joosten, J. G. H.; Levine, Y. K. *Phys. Rev. A* **1990**, *42*, 4820.
- (31) Smeets, J.; Koper, G. J. M.; Ploeg, J. P. M. v. d.; Bedeaux, D. *Langmuir* **1994**, *10*, 1387.
- (32) Withers, I. M.; Dobrynin, A. V.; Berkowitz, M. L.; Rubinstein, M. *J. Chem. Phys.* **2003**, *118*, 4721.
- (33) Koper, G. J. M.; Sager, W. F. C.; Smeets, J.; Bedeaux, D. *J. Phys. Chem.* **1995**, *99*, 13291.
- (34) Munk, P. *John Wiley & Sons: New York* **1989**, 229.
- (35) Dijk, M. A. v.; Joosten, J. G. H.; Levine, Y. K. *J. Phys. Chem.* **1989**, *93*, 2506.
- (36) Hou, M. J.; Kim, M.; Shah, D. O. *J. Colloid Interf. Sci.* **1988**, *123*, 398.
- (37) An, X.; Feng, J.; Shen, W. *J. Phys. Chem.* **1996**, *100*, 16674.

Table of contents entry:



The interaction enthalpy of microemulsion droplets depends on the solvent type, varying from the positive to the negative.

