Transfer of Homologous Alkanols from Water to Fluorocarbon and Hydrocarbon Surfactant Micelles

Masahiro MANABE,* Hideo KAWAMURA,† Gohsuke SUGIHARA,†† and Mitsuru TANAKA††
Department of Industrial Chemistry, Niihama National College of Technology, Niihama, Ehime 792
††Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka 814-01
(Received October 27, 1987)

The critical micelle concentration, cmc, of sodium perfluorooctanoate, SPFO, and sodium dodecyl sulfate, SDS, in the presence of two homologous series of alkanols (1-alkanols and ω-phenyl-1-alkanols) at very low concentrations of the alkanols C_a, was measured by a differential specific conductivity method. The free energy of transfer per CH_2 group in the alkanols from water to the respective micelles, $\Delta G°(CH_2)$, has been estimated from a linear relation of the rate of cmc-decrease, $\Delta cmc/\Delta C_a$, with the number of carbon atoms in the alkyl chain of alkanols. The respective values of $\Delta G°(CH_2)$ obtained for two series of homologues added to a given surfactant are in good agreement with each other: $\Delta G°(CH_2)$ is -1.73 kJ mol^{-1} in the SPFO system and -2.30 kJ mol^{-1} in the SDS system. The former has been found to be smaller in magnitude than the latter. On the basis of $\Delta G°(CH_2)$, a thermodynamic parameter has been proposed which characterizes the degree of modification of a medium from its pure liquid state to surfactant micelles or to interfaces composed of a hydrocarbon or a fluorocarbon.

Fluorocarbons are unique in their phobicity not only to water but also to hydrocarbons. Mixtures of a fluorocarbon and a hydrocarbon exhibit a positive deviation from the ideal solution behavior and there occurs partial miscibility as can be seen, for example, in n-C_4F_{10}–n-C_4H_{10} system.[1] The unique properties have tempted some workers to study the mixed micelle formation of a fluorocarbon surfactant and a hydrocarbon surfactant,[2-8] and the solubilization of hydrocarbon derivatives in fluolocarbon surfactant solutions.[9] One of the interesting results obtained is that the relation of the critical micelle concentration, cmc, with the composition of surfactants gives a maximum,[2-4,7] or a minimum.[8] It has been ascribed to the nonideality of mixing, i.e., to the coexistence of two types of mixed micelles in mutual solution; the regular solution theory has been applied to explain cmc data.[3]

It is known that the standard free-energy change of transfer of some homologous series of hydrocarbon derivatives from water to various environments, such as oil phases, micelles, and interfaces, has a linear dependence on the number of carbon atoms in the homologues; the transfer free energy per CH_2 group, $\Delta G°(CH_2)$, gives information about the interaction of the hydrocarbon chain with the respective environments.[10] However, few studies on $\Delta G°(CH_2)$ between water and fluorocarbon media have so far been made.[11] Such studies will afford a better understanding of the nonideal behavior of mixed surfactant solutions of fluorocarbon and hydrocarbon surfactants.

In the present study, the initial rate of decrease of the cmc of a fluorocarbon surfactant and a hydrocarbon surfactant upon the addition of two homologous series of alkanols has been determined in order to estimate $\Delta G°(CH_2)$ between water and the respective surfactant micelles.

Experimental

Materials. Sodium perfluorooctanoate, SPFO, was prepared as follows. Commercially available perfluorooctanoic acid (P.C.R Research Chemicals, U.S.A.) was recrystallized twice from CCl_4. Its aqueous solution was neutralized with NaOH; then, the crude crystals obtained were recrystallized twice from water and then dried in a vacuum. Sodium dodecyl sulfate, SDS, was synthesized and purified using the same procedure as described elsewhere.[12] Each surfactant gave no minimum around its critical micelle concentration, cmc, in a plot of the surface-tension against concentration. Purchased 1-alkanols (C_2—C_7; Tokyo Kasei, Japan) and ω-phenyl-1-alkanols ($C_6H_5(CH_2)_mOH$: m=1—3; Tokyo Kasei) were used as additives after fractional distillation; the phenylalkanols (m=4, 5: 99%; Aldrich, U.S.A.) were used without further purification. The water for solvent was purified by means of ion exchange and distillation. Its specific conductivity was lower than 2 μS cm^{-1} at 298.15 K.

Conductivity Measurements for cmc Determination. An aqueous solution with a given concentration of each alkanol was prepared and used as a solvent. A portion of the solvent was poured into a conductivity cell (cell constant: 0.4743 cm^{-1}). A concentrated surfactant solution was prepared with the other portion of the solvent, and successively added into the conductivity cell. Upon each addition, the conductivity of the solution was measured on a conductivity metel (Model MY-8; Yanagimoto, Japan). The temperature of the water bath was controlled at 298.15±0.005 K.

Results and Discussion

In order to determine the critical micelle concentration, cmc, of the surfactants in the presence of alkanols, the differential specific conductivity method[2,13] was applied. Figure 1 illustrates the dependence of the differential conductivity, $\Delta\kappa/\Delta C_s$, on the mean concentration of surfactants, $\bar{C}_s$, just around the cmc, in an SPFO–1-hexanol system. At a given concentration of alkanol, C_a, $\Delta\kappa/\Delta C_s$ decreases slowly and

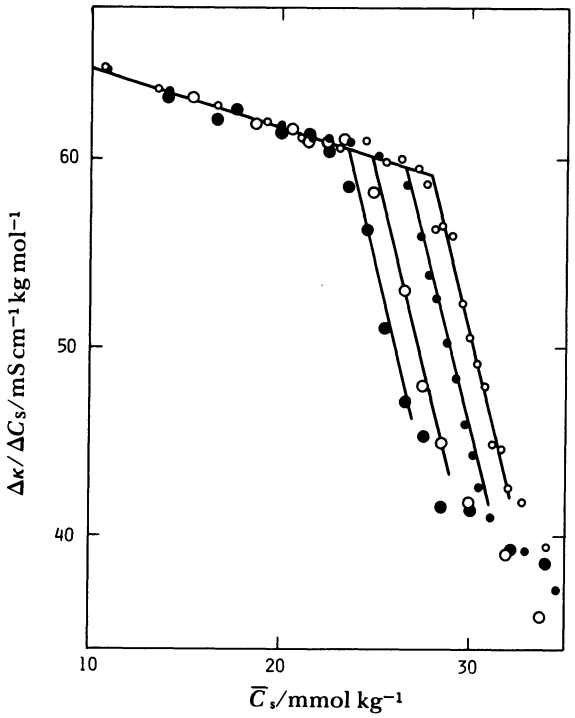

Fig. 1. The dependence of differential specific conductivity on the mean concentration of SPFO. Concentration of 1-hexanol in mmol kg^{-1}: 0 (○); 4.995 (●); 10.60 (○); 15.00 (●).

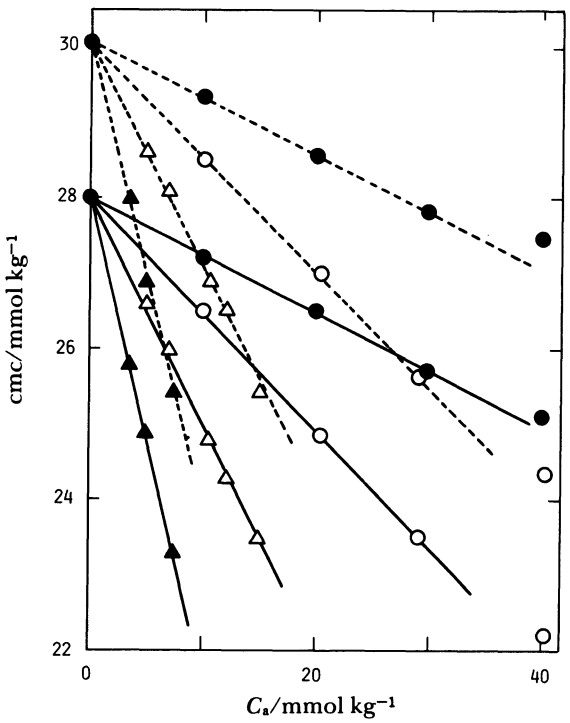

Fig. 2. The dependence of cmc of SPFO on 1-alkanol concentration. cmc determination method: equivalent conductivity (broken line); differential conductivity (solid line). Added 1-alkanols: 1-butanol (●); 1-pentanol (○); 1-hexanol (△); 1-heptanol (▲).

linearly until a break point; then it decreases sharply in a linear fashion whthin a narrow region of $\bar{C}_s$. The value of $\bar{C}_s$ at the intersection of the two straight lines is taken as the cmc. It is apparent that the points of $\Delta\kappa/\Delta C_s$ below the cmc fall on the same line, at any C_a studied, whereas the lines above the cmc are regarded as being parallel to each other. The latter finding indicates that the break remains clear, even if C_a increases; this is in marked contrast to a plot of the equivalent conductivity against the square root of the surfactant concentrations, C_s, (equivalent conductivity method) and a plot of specific conductivity against C_s (specific conductivity method), which are often employed for cmc determinations. In the latter two plots, as is well-known, the break around cmc becomes less distinct with increasing C_a. Therefore, it is claimed that the differential conductivity method is better for a cmc determination than those other conductivity methods, especially in the presence of some additives.

The cmc of SPFO determined by the differential conductivity method and the equivalent conductivity method is plotted in Fig. 2 against C_a of 1-alkanols, where the cmc value by the former method can be ascertained with more accuracy than by the latter method because of the more distinct break in Fig. 1. It is obvious that at a definite C_a of a certain alkanol, the cmc values are different from each other determined by the respective methods: the values are higher in the order of those by the specific, equivalent, and differential conductivity method, although cmc by the specific conductivity method is not shown in Fig. 2. In line with the reported results,[14,15] the cmc decreases linearly with C_a up to a certain C_a; this decreasing tendency becomes more marked with an increase in the alkyl-chain length of alkanols. The limiting slopes, $\Delta cmc/\Delta C_a$, shown by the straight lines, are found to be almost identical, irrespective of the determination methods. The values of $\Delta cmc/\Delta C_a$ estimated from the cmc data by the differential conductivity method are listed in Table 1.

Table 1. $\Delta cmc/\Delta C_a$ and $\Delta G°(CH_2)$ for 1-Alkanols and ω-Phenyl-1-alkanols Added in SDS and SPFO at 298.15 K

	$-\Delta cmc/\Delta C_a$				
m_n	SDS[a]	SPFO	m_p	SDS	SPFO
4	0.028	0.0767	1	0.0667	0.0663
5	0.078	0.155	2	0.113	0.134
6	0.21	0.300	3	0.255	0.258
7	0.53	0.634	4	0.553	0.500
			5	1.40	1.15
$-\Delta G°(CH_2)$[b]	2.45	1.74		2.19[c]	1.73

a) Taken from Ref. 15. b) In kJ mol^{-1} unit. c) Determined at m_p=3—5.

The relation between $\log(-\Delta cmc/\Delta C_a)$ and the

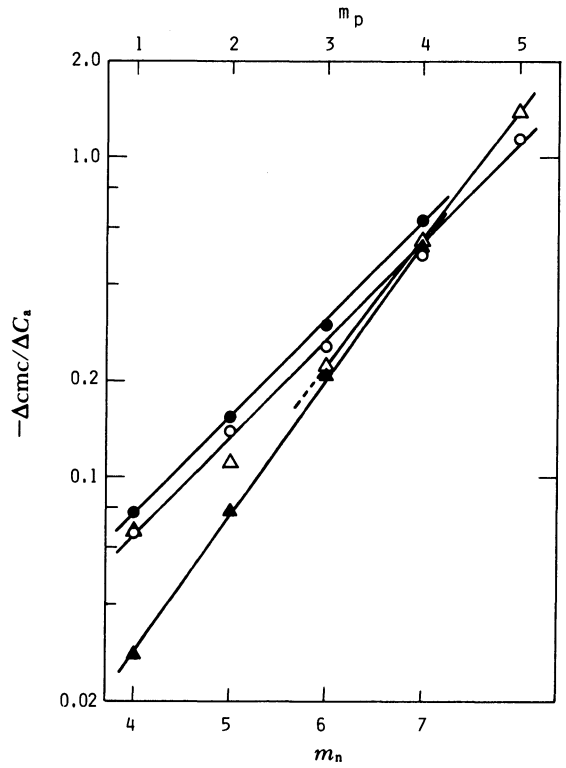

Fig. 3. The dependence of $\log(-\Delta cmc/\Delta C_a)$ on the number of carbon atoms in the alkylchain of added alkanols. Surfactant: SPFO (circle); SDS (triangle). Alkanol: 1-alkanol (closed mark); ω-phenyl-1-alkanol (open mark).

number of carbon atoms in the alkyl chain of added homologous alkanols (denoted by m_n for 1-alkanols, and m_p for ω-phenyl-1-alkanols) is shown in Fig. 3 where literature data for the SDS–1-alkanol systems[15] are also plotted. It is apparent that, as has been known in other systems,[14,15] a linear relation holds in each system, except for some short-chain alkanols (m_p=1, 2). It is perceived that the respective straight lines of 1-alkanols and phenylalkanols for each surfactant are parallel to each other and that the slopes of the straight lines for SPFO are less steep than those for SDS.

It is found that at a given value of $\Delta cmc/\Delta C_a$ for each surfactant, m_p is higher by about 3 than m_n, i.e., $m_p=m_n+3$. This result implies that the phenyl group is hydrophobic and its hydrophobicity corresponds to that of three methylene groups in the alkyl-chain. The difference of 3 is in agreement with that assigned to the phenyl group in a homologous series of sodium alkylbenzenesulfonates by comparison in cmc with homologous sodium alkanesulfonates.[16]

Manabe et al.[17] described the relation between $\Delta cmc/\Delta C_a$ and K_x (partition coefficient of a solubilizate between the bulk water and micelle phases, in mole fraction unit). When C_a is very low, the relation is expressed as

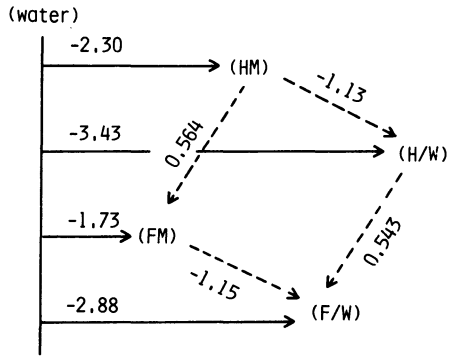

Fig. 4. Free energy of transfer per CH_2 group at 298.15 K. Values are in kJ mol^{-1}. Data for H/W and F/W are taken from Ref. 11.

$$-\Delta cmc/\Delta C_a = (cmc_0/n_w)\theta K_x, \quad (1)$$

where cmc_0, n_w, and θ refer to the cmc in water (in molality unit), the mole number of water, and a constant, respectively. In the SDS–1-alkanol systems (m_n=4—7), the value of θ (0.69,[17] 0.82[18]) was reported to be independent of the chain-length of alkanols. Assuming that θ is constant in each present system, the standard free-energy change of transfer per CH_2 group in the alkanols from the bulk water to micelles, $\Delta G°(CH_2)$, can be calculated through Eq. 1 as

$$\Delta G°(CH_2) = -RT\,d\ln(-\Delta cmc/\Delta C_a)/dm. \quad (2)$$

Here, R, T, and m are the gas constant, the absolute temperature, and the carbon number (m_n or m_p), respectively. The values of $\Delta G°(CH_2)$ calculated by Eq. 2 from the linear relation in Fig. 3 are shown in Table 1. It is noticed that $\Delta G°(CH_2)$ for the respective homologous series with a given surfactant are in agreement, as can also be seen in Fig. 3; also the value for SPFO (mean value, −1.73 kJ mol^{-1}) is smaller in magnitude than that for SDS (−2.30 kJ mol^{-1}). These figures indicate that a hydrocarbon derivative is more difficult to be solubilized in fluorocarbon surfactant micelles than in hydrocarbon surfactant ones. This is consistent with the fact that a liquid hydrocarbon is partially miscible with a liquid fluorocarbon, as observed in the n-C_4H_{10}–n-C_4F_{10} system.[1]

Mukerjee and Handa[11] measured the interfacial tension of dilute aqueous solutions of some homologous sodium alkyl sulfates as well as some sodium perfluoroalkanoates at air-water (A/W), hydrocarbon-water (H/W), and fluorocarbon-water (F/W) interfaces, and estimated the free-energy change for a CH_2 group as well as a CF_2 group in the surfactant molecules transferring from water (W) to each interface. For the CH_2 group, their data are schematically compared in Fig. 4 with the present data for $\Delta G°(CH_2)$ in the transferring process from W to hydrocarbon surfactant micelles (HM) and to fluorocarbon surfactant micelles (FM). Figure 4 suggests that

the oil-water interface has a greater affinity for the CH_2 group than the micelle when both media consist of the same substance (hydrocarbon or fluorocarbon). Further, it is apparent that the difference of the free energy of transfer between HM and H/W (1.13 kJ mol^{-1}) is in agreement with the difference between FM and F/W (1.15 kJ mol^{-1}). In addition, the difference between HM and FM (0.564 kJ mol^{-1}) is also regarded as being identical with that between H/W and F/W (0.543 kJ mol^{-1}). Accordingly, the four broken lines in Fig. 4 form a parallelogram. The parallelogrammic relation suggests that the modification of a type of medium, such as micelle or interface, characterizes a unique affinity for the CH_2 group.

The difference, 0.543 kJ mol^{-1}, between F/W and H/W in Fig. 4 was attributed by Mukerjee and Handa[11] to a nonideality of the mixing of hydrocarbon and fluorocarbon, by a comparison with the following excess free energy. By the regular solution approach, the incremental change per methylene group in the partial molar excess free energy of homologous hydrocarbons dissolved at infinite dilution in perfluorohexane was estimated to be 0.585 kJ mol^{-1}, which was in agreement with the value 0.543 kJ mol^{-1}. It should be noted that in the calculation for the respective free energies, different standard states of the solute were used, i.e., an extrapolated state from a limiting dilution for the adsorption free energy and the pure state of solute for the excess free energy. Then, we will propose an alternative explanation for the thermodynamic relation between the different standard states.

We consider a solute such as a hydrocarbon derivative distributed between two phases, α and β, at mole fractions of the solute, x^α and x^β, in respective phases. At a certain temperature and pressure, the chemical potential of the solute in each phase, μ^α and μ^β, can be expressed on the basis of two different reference systems. The one is that the activity coefficient (γ) of the solute is equal to unity in its pure liquid state (so called, Raoult's reference system) and the other is that the activity coefficient (f) of the same solute approaches unity as the solution becomes more and more dilute (Henry's reference system). Representing standard chemical potentials in, e.g., α phase as $\mu^{\alpha 0}$ and $\mu^{\alpha\ominus}$ by respective reference systems, the chemical potentials can be expressed as

$$\mu^\alpha = \mu^{\alpha 0} + RT\ln(\gamma^\alpha) + RT\ln(x^\alpha)$$
$$= \mu^{\alpha\ominus} + RT\ln(f^\alpha) + RT\ln(x^\alpha)$$

and

$$\mu^\beta = \mu^{\beta 0} + RT\ln(\gamma^\beta) + RT\ln(x^\beta)$$
$$= \mu^{\beta\ominus} + RT\ln(f^\beta) + RT\ln(x^\beta). \quad (3)$$

It should be noticed that in the above equations $\mu^{\alpha 0}$ is identical with $\mu^{\beta 0}$ since they concern the same pure solute. When in equilibrium, $\mu^\alpha=\mu^\beta$; therefore, from Eq. 3,

$$\mu^{\beta 0} - \mu^{\alpha 0} = 0 = -RT\ln(\gamma^\beta/\gamma^\alpha) - RT\ln(x^\beta/x^\alpha)$$

and

$$\mu^{\beta\ominus} - \mu^{\alpha\ominus} = -RT\ln(f^\beta/f^\alpha) - RT\ln(x^\beta/x^\alpha). \quad (4)$$

Under the conditions of infinite dilution of the solute in both phases, both f^α and f^β can be taken to be unity. Form Eq. 4, it follows that

$$\mu^{\beta\ominus} - \mu^{\alpha\ominus} = -RT\ln(x^\beta/x^\alpha) = RT\ln(\gamma^\beta/\gamma^\alpha). \quad (5)$$

This equation reveals a significant point that the standard free energy change, $\mu^{\beta\ominus}-\mu^{\alpha\ominus}$, for an ideal solution based on Henry's system is correlated with the excess free-energy change on Raoult's system.

These considerations can be applied to the present data as follows. The standard free energy of transfer, corresponding to $\mu^{\beta\ominus}-\mu^{\alpha\ominus}$ in Eq. 5, between any pair of media in Fig. 4 is calculated as the difference of $\Delta G°(CH_2)$. The quantity of $\Delta G°(CH_2)$ in the transferring process from water to each medium is denoted by $\Delta G°(CH_2{:}W)$; the values are arranged according to the order of magnitude in Table 2. When the CH_2 group transfers from a hydrocarbon medium to another one, the free energy of transfer, denoted by $\Delta G°(CH_2{:}H)$, may be given as the difference between $\Delta G°(CH_2{:}W)$ and -3.59 kJ mol^{-1} determined from the partition coefficients of homologous 1-alkanols between water and dodecane at infinite dilution at 298.15 K.[19] The values of $\Delta G°(CH_2{:}H)$ are also

Table 2. Thermodynamic Quantities for CH_2 Group in Transfering Processes at 298.15 K

Medium	$-\Delta G°(CH_2{:}W)$ / kJ mol^{-1}	$\Delta G°(CH_2{:}H)$[b] / kJ mol^{-1}	γ^ω	$((RT\ln(\gamma^\omega))/\bar{V})^{1/2}$ / (cal cm^{-3})$^{1/2}$[c]
H	3.59[a]	0	1	0
H/W	3.43	0.040	1.07	1.55
F/W	2.88	0.711	1.33	3.19
A/W	2.59	1.00	1.50	3.80
HM	2.30	1.30	1.69	4.33
FM	1.73	1.86	2.12	5.18
W	0	3.59	4.27	7.20

Notations are defined in text. a) From Ref. 19. b) $\Delta G°(CH_2{:}H)=\Delta G°(CH_2{:}W)-(-3.59)$. c) 1 cal=4.184 J.

shown in Table 2. If the hydrocarbon medium and another one are represented by superscripts h and ω instead of α and β in the above equations, respectively, $\Delta G°(CH_2{:}H)$ can be rewritten along with Eq. 5 as

$$\Delta G°(CH_2{:}H) = \mu^{\omega\ominus} - \mu^{h\ominus} = RT\ln(\gamma^{\omega}/\gamma^{h}). \quad (6)$$

Assuming that the hydrocarbon solution of the CH_2 group is a perfect solution, γ^h as well as f^h may be regarded to be unity. Then, we obtain

$$\Delta G°(CH_2{:}H) = RT\ln(\gamma^{\omega}). \quad (7)$$

This equation is in line with that derived by Butler et al.[20] The values of γ^{ω} calculated by Eq. 7 are listed in Table 2. It is recognized that the medium with a higher value of γ^{ω} has a lower affinity to the CH_2 group. Therefore, the activity coefficient, γ^{ω}, based on Raoult's reference system, is a parameter which numerically characterizes each type of media (the degree of modification of a solvent), such as micelle or interface, in which the CH_2 group is dissolved.

According to the regular solution theory by Hildebrand,[21] the activity coefficient of a solute (γ^R) which is originally related to the energy of mixing is expressed by the quantities, i.e., solubility parameters of a solute (δ_2) and a solvent (δ_1), molar volume of the solute (V_2), and volume fraction of the solvent (ϕ_1), as $RT\ln(\gamma^R)=V_2\phi_1^2(\delta_2-\delta_1)^2$. Present data concerning γ^{ω} and the literal value of the partial molar volume of the CH_2 group, $\overline{V}$, 16.6 $cm^3\,mol^{-1}$,[22] which is the incremental change of partial molar volumes of homologous alkanols in a hydrocarbon, allow us to estimate the quantity $(RT\ln(\gamma^{\omega})/\overline{V})^{1/2}$, which corresponds to the difference of the solubility parameter, $|\delta_2-\delta_1|$. The values of $|\delta_2-\delta_1|$ for some representative substances (hexane($\delta_1=\delta_2=7.3$),[23] perfluorohexane ($\delta_1=5.9$),[23] and water ($\delta_1=24$)[24]) are 0, 1.4, and 16.7, respectivelly. It is seen that this order is consistent with that of $(RT\ln(\gamma^{\omega})/\overline{V})^{1/2}$ in Table 2. In the regular solution theory, the activity coefficient of a solute depends only on the properties of the solute and solvent in their pure states. However, for a given solute (CH_2 group), γ^{ω} reflects the characteristics of its solvent not only in the pure state but also in the modified states such as micelle or interface. In this respect, it is claimed that γ^{ω} is more useful than γ^R in the regular solution approach. Further, the parallelogram relation in Fig. 4 suggests that the modification of the solvent is uniquely determined and the degree of modification is reflected on γ^{ω}.

Thanks are due for the partial support by a research grant from the Ministry of Education, Culture and Science (No. 60470011).

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