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Physicochemical investigations on microemulsification of eucalyptol and water in presence of polyoxyethylene (4) lauryl ether (Brij-30) and ethanol

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Abstract

The microemulsification of eucalyptol/polyoxyethylene(4)lauryl ether (Brij-30)/ethanol/water has been investigated. The phase behaviours of the mixed system in pseudoternary and tetrahedral representations have been examined to understand the topological nature of the multicomponent mixtures. Phase volumes of the heterogeneous combinations have been estimated to understand the mixing efficacy of the combinations. Shear viscosities of different monophasic compositions have been measured at different shear rates and temperatures, and the activation parameters for the viscous flow have been evaluated. The dimensions of the nanodispersions of w/o and o/w types, their diffusion coefficients and the polydispersity have been determined by the DLS method. The energetics of solubilisation (dissolution) of water in oil + Brij-30 + ethanol as well as oil in water + Brij-30 + ethanol forming w/o and o/w microemulsions, respectively, have been calorimetrically determined. Considering the phase separation point to be the point of maximum solubility, the energetic parameters (enthalpy, free energy and entropy) of the microemulsification process have been estimated. © 2001 Published by Elsevier Science B.V.

Keywords: Microemulsion; Eucalyptol; Brij-30; Ethanol; Shear viscosity; Energetics of formation; Hydrodynamic radius

1. Introduction

Eucalyptol (or cineole), 1,3,3-trimethyl-2-oxabicyclo[2,2,2]-octane (Gennavo, 1990), the major component of eucalyptus oil is a volatile, colourless liquid having characteristic odour and taste of punel. It has several uses in pharmaceutical and industrial preparations. It is a flavouring agent and an expectorant (in chronic bronchitis), has bactericidal properties and finds quasi-pharmaceutical applications such as disinfecting wounds and cleaning congested nasal passage (Atal and Kapur, 1982)

For quick and smooth applications, it is advantageous to microemulsify plant and vegetable oils and water. Though preparation of microemul-

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sions with these types of oils is a difficult problem, it can be achieved in presence of suitable emulsifiers (amphiphiles) (The Wealth of India: A Dictionary of Indian Raw Materials & Industrial Products; CSIR, 1952; Kunieda and Shinoda, 1983; Das et al., 1989, 1991; Paul and Moulik, 1991; Paul et al., 1991; Mitra et al., 1994, 1996; Gupta et al., 1995; Mukhopadhyay et al., 1997). If the ingredients are suitably chosen, emulsification in microdispersed level may result. When the ingredients of microemulsion are of biological origin or biocompatible in nature, they are termed 'Biological Microemulsion'.

Usually, in addition to a surfactant a cosurfactant is required to mix plant or vegetable oil and water to achieve microemulsification, which is a potential field of study. We herein present the results of mutual mixing of eucalyptol, water, Brij-30 and ethanol forming stable isotropic dispersions in terms of phase behaviour, consistency, droplet dimension and energetics by measuring solubility limit, shear viscosity, scattering of light and heat of solubilisation. Quantification of the results has been attempted. It may be mentioned that comparable microemulsions of the types, isopropylmyristate/polysorbate/sorbitol/water and water/lecithin/alcohol/isopropylmyristate have been physicochemically studied (Attwood and Ktistis, 1989; Ktistis, 1990; Attwood et al., 1992; Aboofazeli and Lawrence, 1993).

2. Materials and methods

2.1. Materials

The eucalyptol (Eu) was obtained from Fluka, USA. Its boiling point, refractive index and density agreed nicely with literature value and the material was used without further purification. The surfactant polyoxyethylene (4) lauryl ether (Brij-30 or Bj-30) was obtained from Aldrich, USA and the cosurfactant ethanol (EtOH) was the product of Bengal Chemicals Pvt. Ltd., India. It was distilled following standard procedure for purification. Doubly distilled water was used in all preparations.

2.2. Methods

2.2.1. Preparation of microemulsion (phase behaviour)

Microemulsion was prepared in two ways. In the first, Bj-30 and ethanol were mixed at a constant mass ratio and was dissolved in Eu forming solutions of different concentrations. They were taken in different stoppered test tubes and were titrated under stirring with water at a constant temperature until the point of turbidity or phase separation. In the second, the Bj-30-ethanol composite was dissolved in water at different concentrations and titrated with Eu at a constant temperature again until just turbid under the condition of stirring. For all the samples, sufficient time for equilibration was allowed to examine the end point, which was monitored visually against a dark background illuminating the sample with white light. The experiments were duplicated or triplicated to check reproducibility. For estimating the phase volume of the multiphasic regions, several compositions of the quaternary system of Eu/Bj-30/EtOH/water were prepared in stoppered graduated test tubes and were mixed well and, allowed time for equilibration. They evidenced formation of two or three phases, the volumes of which were directly read from the graduations on the test tubes.

2.2.2. Viscosity measurements

For viscosity measurements, compositions of the mixed systems were chosen from the monophasic region in the phase diagram in such a way that they were either w/o or o/w types. These compositions were above the boundary of the heterogeneous phase and were clear and viscous. The viscosities of the chosen compositions were measured at different shear rates and temperatures using a Haake (Germany) Viscometer (Rotovisco RV20, measuring system M_5, sensor system N_v). During measurement, shear rates (D) of 27–2700 s^{-1} were applied (by a rotating head inserted into a cup containing 12–15 ml of the sample solution) and the corresponding shear stress (τ) were monitored. The viscosity, η was then obtained from the relation, $\eta = \tau / D$. The shear viscosity of other microemulsion systems were obtained following similar procedure (Mitra et al., 1994, 1996; Majhi and Moulik, 1999).

2.2.3. Dynamic light scattering measurements

The droplet dimension of nanodispersions was measured by the DLS method at different temperatures. The experiments were performed at 90° in a dynamic light scattering spectrophotometer (Model DLS 700, Otsuka Electronics Co. Ltd., Japan) using a Neon laser of wavelength 632 nm and placing the sample tube in the thermostated chamber of the goniometer. The experimented solutions were repeatedly (three to four times) filtered through millipore filters of pore size 0.45 μm to remove extraneous particles. The intensity data were processed using the instrument's software to obtain the hydrodynamic diameter (d_h), the polydispersity index (PDI, which is the ratio of the standard deviation (S.D.) in d_h and the average d_h) and the diffusion coefficient (D) of the dispersed droplets. This is a standard procedure for the DLS measurements (Moulik et al., 1999a,b; Roy and Moulik, 2000).

2.2.4. Calorimetric measurements

The heat of solubilisation (or dissolution) was measured in a TRONAC 458 Isoperibol titration calorimeter, USA using the procedure described earlier (Das et al., 1992; Mukherjee and Moulik, 1993). In the actual experiment, 3 ml of either (Bj-30 + EtOH + Eu) or (Bj-30 + EtOH + water) was taken in the 4-ml capacity calorimetric vessel and was then dipped into the constant temperature bath of the calorimeter maintained at a temperature of 303 ± 0.0002 K. After the attainment of temperature equilibrium, the solution was titrated either with water or oil (Eu) by a power-driven burette up to the point of phase separation known from the constructed phase diagram. The associated heat changes manifested in millivolts were recorded with time on a Houston Omniscribe strip chart recorder. The specific heat of the final solution was also determined by supplying a known amount of heat using a calibrated heater and recording the rise in temperature in millivolts on the strip chart recorder. The procedure adopted for the estimation of heat and calculation of enthalpy and entropy were the same as done earlier (Das et al., 1992; Mukherjee and Moulik, 1993; Moulik and Ray, 1994; Ray and Moulik, 1994; Majhi and Moulik, 1999). All the experiments were duplicated to check reproducibility. The calorimeter functioned within the accuracy of ± 2% on 2 cal. The S.D.s of the measurements were ± 4.1%.

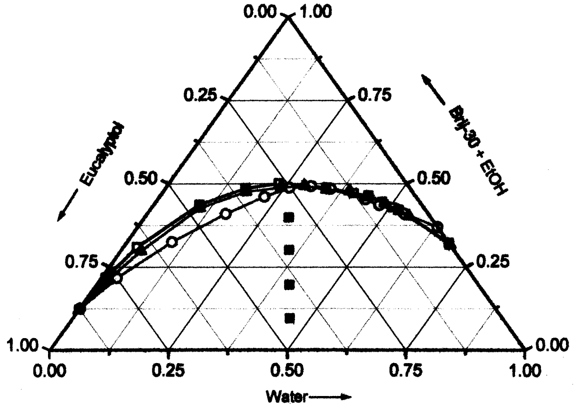

Fig. 1. Pseudoternary phase diagrams of the quaternary system of Eu/Bj-30/EtOH/water at 303 K. □, ○ and ▲ represent 1:1, 2:1 and 1:2 of Bj-30:EtOH ratio (w/w), respectively. ■ represents the compositions for the phase volume study. Scale magnitudes are reduced by 1/100th in the plot.

3. Results and discussion

3.1. Phase behaviours

The pseudoternary phase diagrams represented in Fig. 1 in triangular co-ordinates at 2:1, 1:1 and 1:2 surfactant (s) and cosurfactant (c) weight ratios are virtually of similar types; the demarcation boundary curves between the homogeneous and heterogeneous zones are on the whole symmetrical (Aboofazeli and Lawrence, 1993). Of course, the 1:1 (w/w) s:c containing system has produced a minorly greater monophasic area and detailed property study at this composition has been, therefore, made. The combined phase forming results are represented in tetrahedral representation in Fig. 2. The interior of the hatched and horn like enclosure in the Fig. 2 represents immiscible heterogeneous phase; the clear exterior region is monophasic. The filled area on the Eu

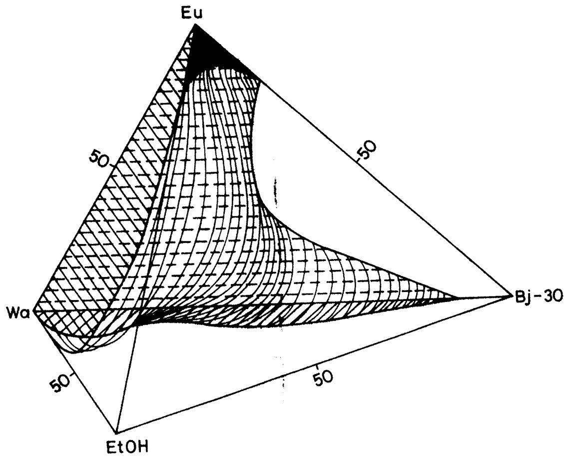

Fig. 2. Composite tetrahedral representation of phase behaviours of the quaternary system of Eu/Bj-30/EtOH/Wa at 303 K. Each triangular face plane represents a ternary system. The caged volume is biphasic, the exterior is monophasic.

Table 1
Phase volumes and nature of the Eu/(Bj-30 + EtOH)/water system at 1:1 (w/w) Brij-30:EtOH at 303 K

Composition[a] (wt.%)	Lower (cc)	Middle (cc)	Upper (cc)
45/10/45	0.490 (t)	–	0.510 (c)
40/20/40	0.306 (c)	0.306 (t)	0.388 (c)
35/30/35	0.354 (c)	–	0.646 (c)
30/40/30	0.271 (c)	–	0.729 (c)

[a] The sequence in composition represents Eu/(Bj-30 + EtOH)/water in mass%.
c = clear; t = turbid.

corner is triphasic. This is a distinct phase forming behaviour of the Eu/Bj-30/EtOH/water system. Distinct phase behaviours of eucalyptus oil/Tween-20/*n*-BuOH or cinnamic alcohol/water system has been reported in a recent publication (Majhi and Moulik, 1999). For the water/polysorbate/sorbitol/isopropylmyristate and water/phospholipid/alkanol/isopropyl myristate systems, very small w/o microemulsion zones have been reported (Ktistis, 1990; Aboofazeli and Lawrence, 1993).

For the determination of the phase volume ratios, samples were chosen from the heterogeneous zone, i.e. below the phase boundary line of Fig. 1 at 1:1 oil:water mass ratio (shown in full squares in the figure). After equilibration, the different layers formed in most of the samples were clear. The lower and middle phase of the first and second samples, respectively, were turbid. One of the compositions produced three phases with nearly equal volume proportions. It was observed that microemulsions of fair proportions were produced in the studied mixtures (Majhi and Moulik, 1999). The results are presented in Table 1. Depending on the requirement, similar phase forming compositions could be examined at other s:c ratios to understand the extents of their formation.

3.2. Shear viscosity

The shear rate dependent viscosity of the preparations at 1:1 s:c ratio at different temperatures were investigated in the temperature range of 20° between 288 and 308 K(Mitra et al., 1994; Kar and Moulik, 1995; Ray and Moulik, 1995; Majhi and Moulik, 1999; Acharya et al., 2001). The studied samples withstood the temperature change without phase separation. The results are graphically represented in Fig. 3. It is seen that the viscosity decreases with the shear rate, i.e. the sample undergoes shear thinning (Mitra et al., 1994). After the shear rate of 351 s^{-1}, the η increases with temperature. This is due to increased disorganisation within the system with increasing temperature. A minimum at 20° and a maximum at 25 °C were observed for all the shear rates. Shear thinning and temperature induced viscosity variations of comparable types were also observed for microemulsions with eucalyptus oil (Majhi and Moulik, 1999) instead of Eu.

The activation enthalpy ΔH^* (taken to be equivalent to the activation energy, ΔE^*) for the viscous flow was estimated according to the equation:

$$\eta = \left(\frac{hN}{V}\right) e^{\Delta H^*/RT} e^{-\Delta S^*/R} \tag{1}$$

using it in the logarithmic form,

$$\ln \eta = \left[\ln\left(\frac{hN}{V}\right) - \frac{\Delta S^*}{R}\right] + \frac{\Delta H^*}{RT} \tag{2}$$

where h, N, V and ΔS^* are Planck's constant, Avogadro number, molar volume and entropy of activation, respectively; the other terms have their usual significance. The first term on the right hand side of Eq. (2) was considered to be constant so that a plot between $\ln \eta$ and T^{-1} should have yielded ΔH^* from the slope. Such plots are non-linear (Fig. 4).

The $\ln \eta$ was expressed in terms of a second-degree polynomial (Eq. (3)), and the ΔH^* was obtained from its derivative with respect to temperature as shown in Eq. (4).

$$\ln \eta = a + bT + cT^2 \tag{3}$$

Thus,

$$\frac{\mathrm{d} \ln \eta}{\mathrm{d}T} = -\frac{\Delta H^*}{RT^2} = b + 2cT \tag{4}$$

The fitting parameters a, b and c were obtained by the method of computation and ΔH^* at different temperatures were then calculated.

The change in the heat capacity, ΔCp was obtained from the relation,

$$\Delta Cp = \frac{\mathrm{d}(\Delta H^*)}{\mathrm{d}T} = -2RT(b + 3cT) \tag{5}$$

The Gibbs free energy for activation, ΔG^* was evaluated from the relation,

$$\Delta G^* = RT \ln\frac{\eta V}{hN} \tag{6}$$

The entropy of activation, ΔS^* then followed from the relation,

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \tag{7}$$

The evaluated activation parameters for the viscous flow of the studied microemulsion compositions are presented in Table 2. The results reveal both increase and decrease of ΔH^* and ΔS^* with temperature depending on the system composition. Representative diagrams are presented in Figs. 5–7. Increase or decrease in ΔH^* and ΔS^* with temperature suggests ordering (organisation) or disordering (disorganisation) of the flowing fluid under a given shearing rate.

The temperature dependence of the Gibbs free energy of activation has shown both maxima and minima which is a consequence of thickening and thinning of the sample under study. A definite

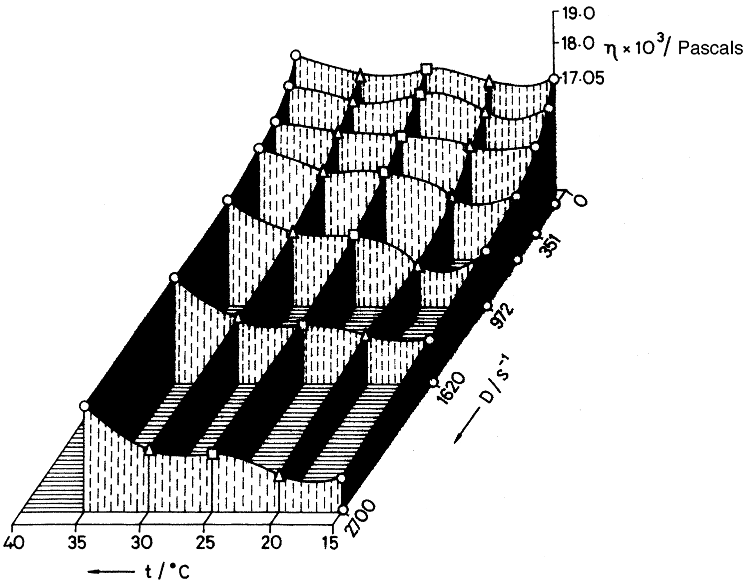

Fig. 3. Interdependence of shear viscosity, shear rate and temperature for the Eu/Bj-30/EtOH/Wa system at Bj-30:EtOH = 1:1. The wt.% composition of the system is 18/25/25/32.

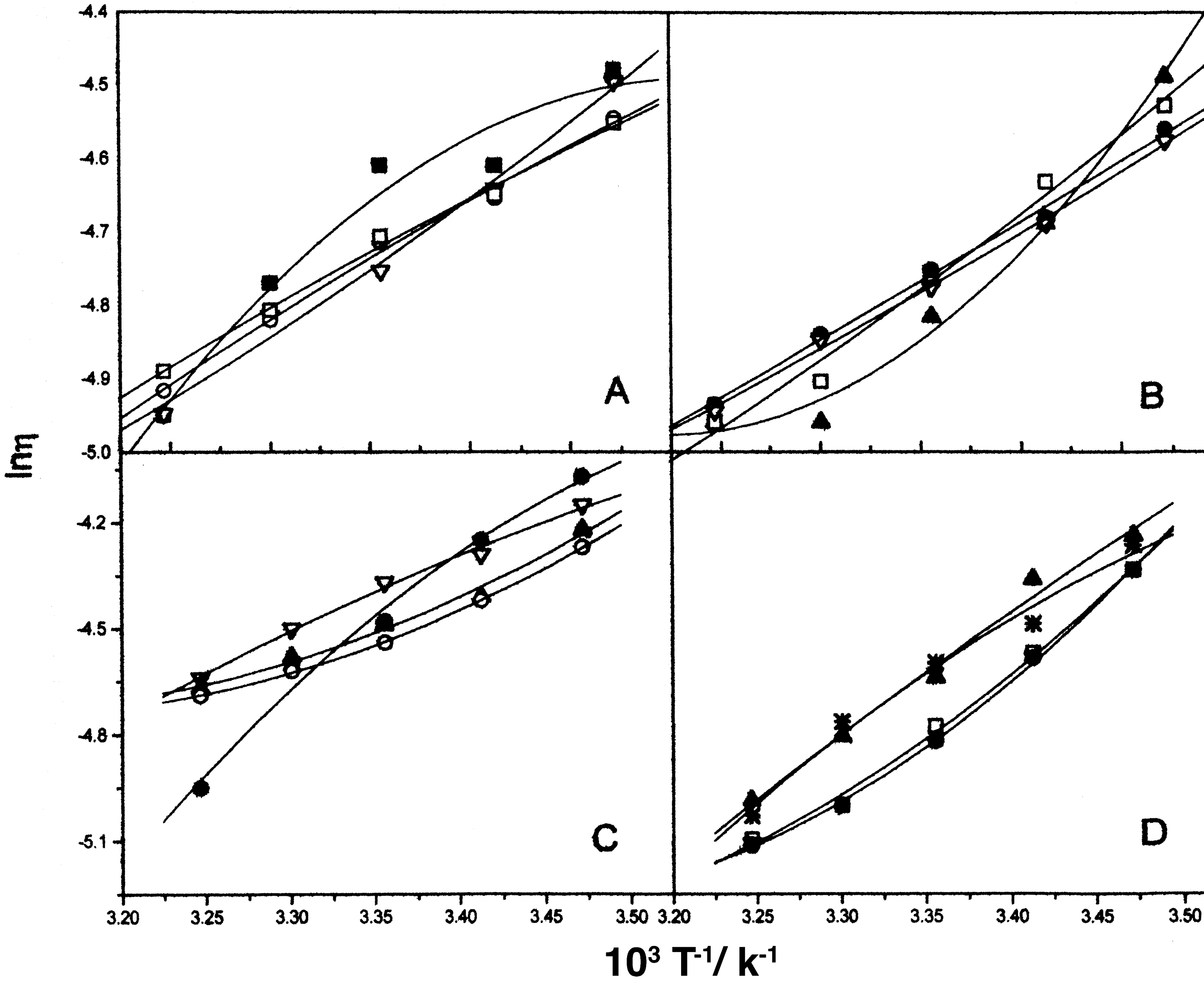

Fig. 4. The plot of ln η vs. T^{-1} for the quaternary system of Eu/Bi-30/EtOH/Wa at four compositions. (A) wt.% composition, 45/22.5/22.5/10, ■, ▽, ○

Table 2
The temperature dependence activation parameters for the mixed eucalyptol/(Brij-30 + EtOH) (1:1)/water at different shear rates

Shear rate (log D)	Temperature (K)	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	ΔCp (J mol^{-1} K^{-1})
Composition (wt.%); 45/45/10 as Eu/(Bj 30 + EtOH)/water					
2.10	288	4.9	14.4	−32.9	1059
	293	10.4	14.3	−13.4	1131
	298	16.3	14.6	5.6	1206
	303	22.5	14.4	26.5	1282
	308	29.1	14.2	48.3	1361
2.55	288	16.7	14.4	8.2	−81
	293	16.3	14.3	6.9	−92
	298	15.8	14.2	5.3	−105
	303	15.2	14.3	3.1	−118
	308	14.6	14.2	1.4	−130
2.99	288	10.6	14.3	−12.7	271
	293	12.0	14.2	−7.7	286
	298	13.4	14.3	−3.0	301
	303	15.0	14.3	2.3	317
	308	16.6	14.3	7.5	333
3.43	288	11.6	14.2	−9.2	81
	293	12.0	14.2	−7.7	82
	298	12.4	14.3	−6.5	83
	303	12.8	14.3	−5.0	85
	308	13.3	14.4	−3.6	86
Composition (wt.%); 31/50/19 as Eu/(Bj 30 + EtOH)/water					
2.10	288	39.9	14.7	87.5	−1614
	293	31.5	14.3	58.6	−1743
	298	22.5	14.2	27.8	−1874
	303	12.8	14.0	−4.0	−2009
	308	2.4	14.2	−38.4	−2148
2.55	288	23.5	14.6	31.1	−231
	293	22.3	14.5	26.7	−256
	298	21.0	14.4	22.2	−281
	303	19.5	14.1	17.7	−308
	308	17.9	14.2	12.0	−335
2.99	288	17.3	14.5	9.8	−37.5
	293	17.1	14.4	9.3	−46.5
	298	16.8	14.4	8.3	−55.8
	303	16.5	14.3	7.2	−65.4
	308	16.2	14.3	6.2	−75.2
3.43	288	17.8	14.4	11.8	−113
	293	17.2	14.3	9.8	−127
	298	16.5	14.3	7.5	−142
	303	15.8	14.3	4.9	−158
	308	15.0	14.3	2.3	−173
Composition (wt.%); 18/50/32 as Eu/(Bj-30 + EtOH)/water					
2.10	288	20.6	15.4	18.1	1010
	293	25.8	15.2	36.2	1073
	298	31.3	14.9	55.1	1138
	303	37.2	14.8	73.8	1205
	308	43.4	14.2	94.8	1273
2.55	288	14.4	15.2	-2.5	297
	293	16.0	15.1	3.0	313
	298	17.6	15.2	8.1	329
	303	19.3	15.1	13.8	345
	308	21.0	15.0	19.7	362
2.99	288	39.3	15.0	84.3	−594
	293	37.1	14.8	76.0	−644

Table 2 *(Continued)*

Shear rate (log D)	Temperature (K)	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	ΔCp (J mol^{-1} K^{-1})
	298	15.4	14.7	2.1	−741
	303	11.5	14.8	−10.7	−796
	308	7.4	14.8	−24.2	−853
Composition (wt.%); 9/46/45 as Eu/(Bj-30+EtOH)/water					
2.10	288	19.3	15.3	13.9	134
	293	20.0	15.4	15.7	136
	298	20.7	15.1	18.6	139
	303	21.4	15.1	20.7	141
	308	22.1	15.0	23.0	143
2.55	288	14.0	15.3	−4.5	491
	293	16.5	15.1	4.7	521
	298	19.2	15.2	13.4	551
	303	22.0	15.2	22.7	581
	308	25.0	14.9	32.8	613
2.99	288	26.9	15.2	40.9	−562
	293	24.0	15.0	30.8	−611
	298	20.8	14.9	19.9	−662
	303	17.4	14.7	8.7	−714
	308	13.7	14.8	−3.6	−768
3.43	288	29.0	15.2	48.2	−744
	293	25.2	15.0	34.8	−807
	298	21.0	14.8	20.7	−872
	303	16.5	14.7	5.6	−938
	308	11.6	14.8	−10.4	−1006

System compositions as Eu/(Bj-30+EtOH)/water in mass%.

trend in the ΔG^* with the thermal condition of the system has not been observed. The trends in the ΔG^* values for the coconut oil/Brij-52/ethanol or isopropanol/water system did not show maximum or minimum (Acharya et al., 2001). The present system has speciality in the above regard.

The positive and negative ΔCp values support increment and decrement in ΔH^* with temperature; their magnitudes depend on the system composition and the shear rate. The results on the whole are reflections of the complexity of the system and reveal their internal ordered/disordered conditions. These informations are required for their uses in practical conditions where shear thinning of a preparation is advantageous for application on a surface wherein it can withstand rise in temperature if its consistency increases with temperature elevation.

The ΔG^* values at the studied temperatures are all very close. They vary nearly within 1 U whereas the ΔH^* and ΔS^* vary considerably. Thus, for a virtually invariant ΔG^* according to the Gibbs equation ($\Delta H^* = \Delta G^* + T\Delta S^*$), ΔH^* and ΔS^* should linearly compensate each other. In Fig. 8, compensation plots between ΔH^* and ΔS^* are shown for the four compositions studied at different shear rates. The plots are excellently linear with very good correlations. The compensation temperatures obtained from the slopes of the linear courses for all the systems is 298 K. The compensation temperature refers to an overall temperature that is required to fit the ΔH^* and ΔS^* data into a linear correlation. In the present case, it is close to the average of the experimented temperatures, 294 K. A compensation temperature of 312 K was realised for the coconut oil/Brij-52/ethanol or isopropanol/water system (Acharya et al., 2001) vis-à-vis an average experimented temperature 308 K.

3.3. Dynamic light scattering

The DLS results obtained for the five compositions of the system under investigation are presented in Table 3. Except for the fourth, the diameter (*d*) of the dispersed droplets has increased with temperature by the process of coalescence or fusion, i.e. the system has proceeded towards instability. On the oil dispersion side (particularly for the fourth composition), the change in *d* with temperature has a decreasing trend whereas for the last sample *d* has slightly increased over a temperature range of 10°. The polydispersity indices are all reasonably high; the preparations are appreciably polydisperse (monodisperse samples give polydispersity index of 0.1). The diffusion coefficients (*D*) are inversely proportional to *d* since they are controlled by the Stokes–Einstein equation,

$$D = \frac{kT}{3\pi\eta d} \tag{8}$$

where *k*, *T* and *η* are the Boltzman constant, absolute temperature and viscosity coefficient of the medium, respectively.

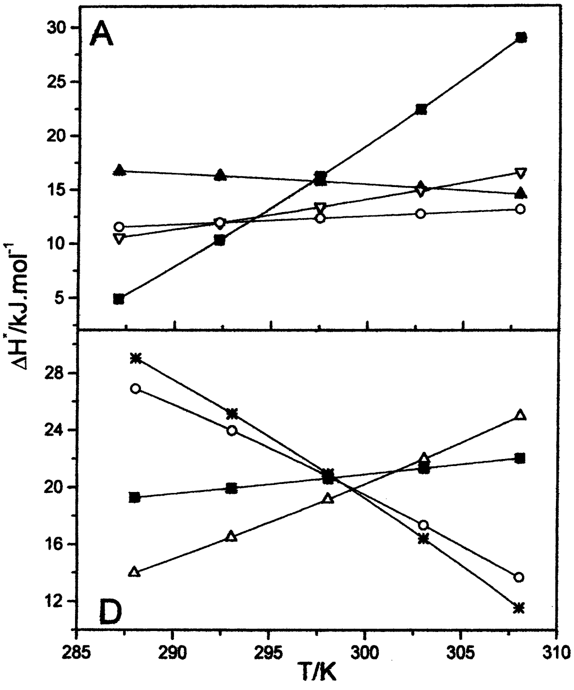

Fig. 5. The plot of ΔH^* vs. T for the quaternary system of Eu/Bj-30/EtOH/Wa at two compositions. (A) wt.% composition, 45/22.5/22.5/10. ■, ▲, ▽ and ○ are at $\log D = 2.10$, 2.55, 2.99 and 3.43, respectively. (D) wt.% composition, 9/23/23/45. ■, △, ○ and ★ are at $\log D = 2.10$, 2.55, 2.99 and 3.43, respectively.

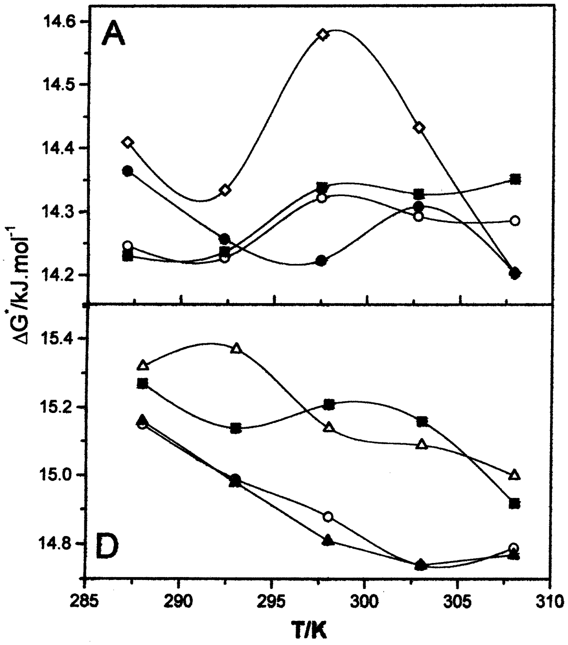

Fig. 6. ΔG^*–T profile for the system, Eu/Bj-30/EtOH/Wa at two compositions. (A) wt.% composition, 45/22.5/22.5/10. ◇, ●, ○ and ■ are at $\log D = 2.10$, 2.55, 2.99 and 3.43, respectively. (D) wt.% composition, 9/23/23/45. △, ■, ○ and ★ are at $\log D = 2.10$, 2.55, 2.99 and 3.43, respectively.

In the case of coconut oil/Brij-52/ethanol or isopropanol/water system, the *d* and *D* have shown both maxima and minima in their temperature profiles (Acharya et al., 2001). Comparable dimensions of oil dispersions in isopropylmyristate/polysorbate/sorbitol/water have been reported by Attwood et al. (Attwood and Ktistis, 1989; Attwood et al., 1992).

3.4. Calorimetry

The thermodynamic informations of the solubilisation of water in oil/amphiphile and that of oil in water/amphiphile media forming microemulsions are presented in Table 4. The compositions indicate the types of system produced by the process of dissolution. The w/o types ended up with release of heat (exothermic process) whereas o/w types were endothermic. Considering maximum addition levels of either water or oil to be the solubility limit (like solubility of a solute, herein, the excess unmixed water goes into a separate phase), the standard Gibbs free energy of solution (ΔG_s^0) was obtained from the relation (Majhi and Moulik, 1999),

$$\Delta G_s^0 = -RT \ln X_d \tag{9}$$

where X_d is the mole fraction of the dispersed phase.

The standard state was the hypothetical state of unit mole fraction where the solubilisate (solute, here water) is in the state of unit activity. The standard enthalpy change ΔH_s^0 for the dissolution process was obtained from the calorimetric measurements.

The standard entropy of solution ΔS_s^0 then followed from the relation,

$$\Delta S_s^0 = \frac{\Delta H_s^0 - \Delta G_s^0}{T} \tag{10}$$

The ΔG_s^0 values are all positive, the dissolution process is non-spontaneous which is expected (Das et al., 1992; Ray et al., 1994; Majhi and Moulik, 1999; Acharya et al., 2001). The ΔS_s^0 are all negative and of reasonable magnitudes. The dispersed droplets of either water or oil are sur-

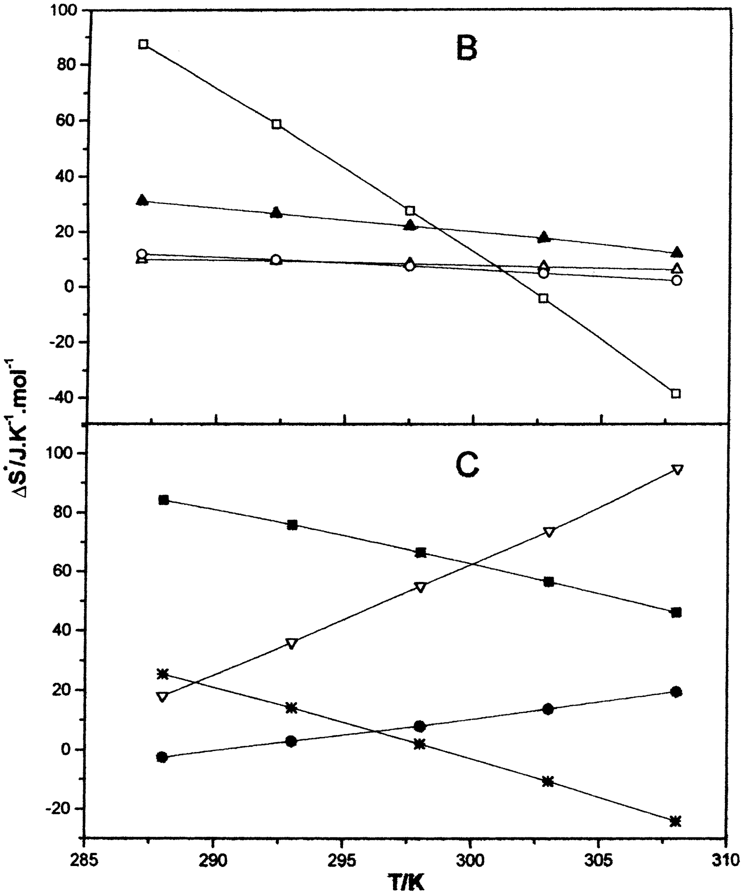

Fig. 7. ΔS^*-T profile for the system, Eu/Bj-30/EtOH/Wa at two compositions. (B) wt.% composition, 31/25/25/19. □, ▲, ▽ and ○ are at log $D = 2.10$, 2.55, 2.99 and 3.43, respectively. (C) wt.% composition, 18/25/25/32. ▽, ●, ■ and ★ are at log $D = 2.10$, 2.55, 2.99 and 3.43, respectively.

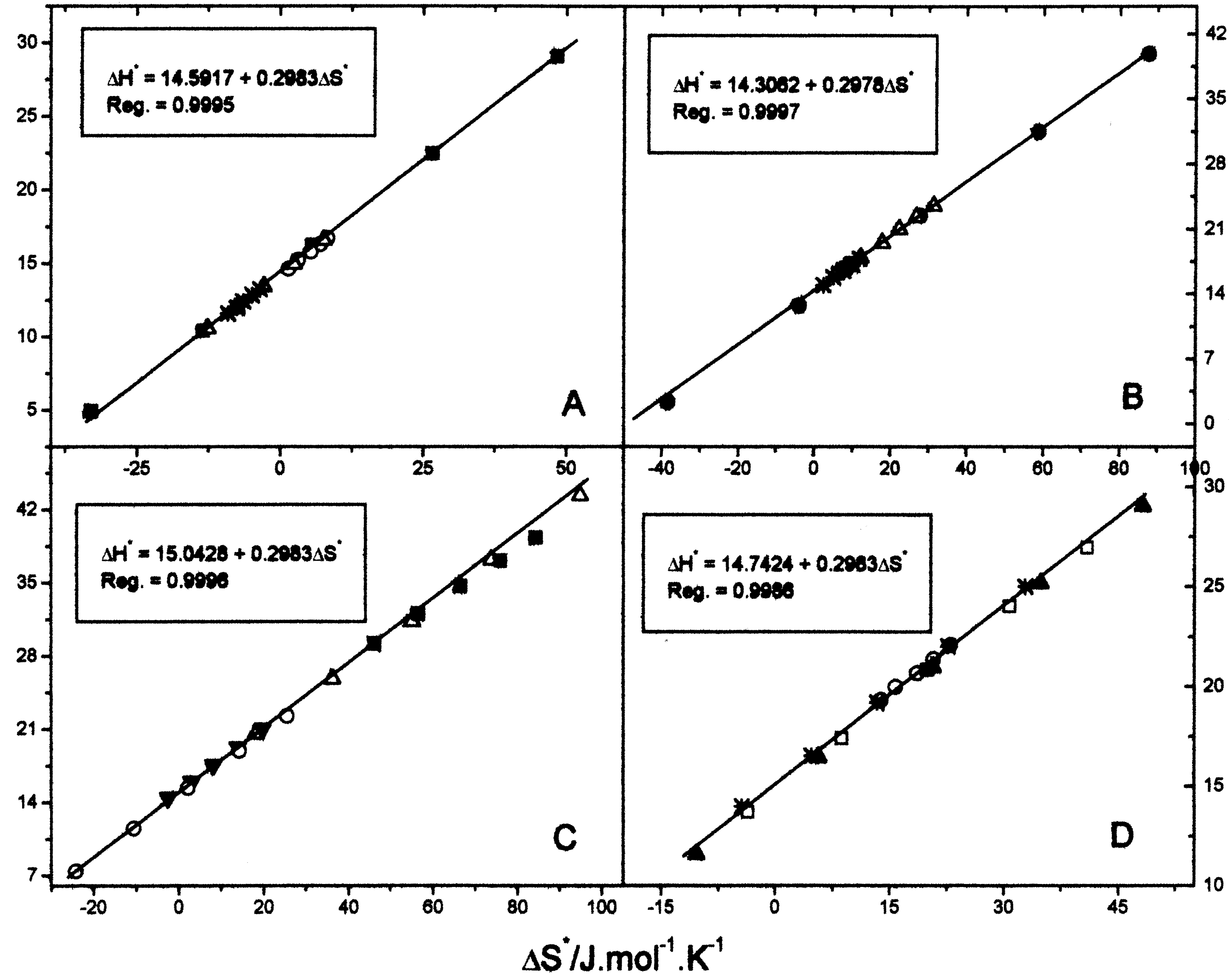

Fig. 8. The ΔH^* and ΔS^* compensation plot for the quaternary system, Eu/Bj-30/EtOH/Wa. (A) wt.% composition, 45/22.5/22.5/10. ■, ○, ▽ and

Table 3
DLS results on the eucalyptol/(Brij-30 + EtOH) (1:1)/water microemulsion systems at different temperatures

Composition[a] (wt.%)	Temperature (K)	Diameter (d) (nm)	Polydispersity index (PDI)	Diffusion coefficient $(D) \times 10^8$ (cm^2 s^{-1})
45/45/10	293	8.0	0.134	5.42
	298	30.2	0.034	1.49
	308	34.6	0.980	1.58
31/50/19	293	3.6	0.732	9.23
	298	13.4	0.823	3.70
	308	22.5	0.848	3.32
18/50/32	298	20.3	0.350	1.64
	308	64.5	0.398	0.65
9/46/45	293	13.1	1.052	1.78
	298	10.8	0.772	2.69
	308	7.2	0.575	5.30
3/39/58	298	0.8	0.565	0.30
	308	1.2	0.429	0.26

[a] The sequence represents Eu/(Bj-30 + EtOH)/water.

Table 4
Energetics of microemulsification of oil and water by calorimetry at 303 K

Composition[a] (wt.%)	Water added (10^{-3} mol)	Oil (Eu) added (10^{-3} mol)	ΔH_s^0 (kJ mol^{-1})	ΔG_s^0 (kJ mol^{-1})	ΔS_s^0 (J K^{-1} mol^{-1})
62/34/4	6.11	–	−1.09	3.89	−16.44
43/45/12	20.0	–	−1.06	2.04	−10.23
32/49/19	34.0	–	−0.89	1.43	−7.66
25/50/25	48.62	–	−0.67	1.12	−5.91
25/50/25	–	5.81	0.84	6.53	−18.78
17/49/34	–	3.59	1.31	7.96	−21.95
12.6/47.1/40.3	–	2.58	1.71	8.99	−24.03
6.5/42.8/50.6	–	1.26	2.33	11.04	−28.75

[a] Final composition having the sequence Eu/(Bj-30 + EtOH)/water.

rounded by a layer of amphiphiles in the dispersing medium in an organised state so that the entropy of the process is negative. In this event, the oil dispersed system is more stabilised/organised than the water dispersed case. Negative entropy of dispersion was also reported on other w/o or o/w microemulsion forming systems (Majhi and Moulik, 1999; Acharya et al., 2001)

In Fig. 9, the enthalpies of solution of both water and oil in amphiphile/oil and amphiphile/water, respectively, forming microemulsions are presented along the triangular phase boundary curve. The results for the w/o compositions fall below the plane of the phase triangle since the formation process was exothermic whereas the formation of the o/w type was endothermic and the results are projected above the plane of the phase triangle. The zero enthalpy condition virtually corresponds to the composition 25/50/25 as Eu/(Bj-30 + EtOH) (1:1 w/w)/water. Compared with the exothermic enthalpy, the endothermic enthalpy of microemulsification is sharper. Similar graphical representation of the enthalpy of microemulsification of both water and oil was reported for the system containing eucalyptus oil in place of Eu (Majhi and Moulik, 1999).

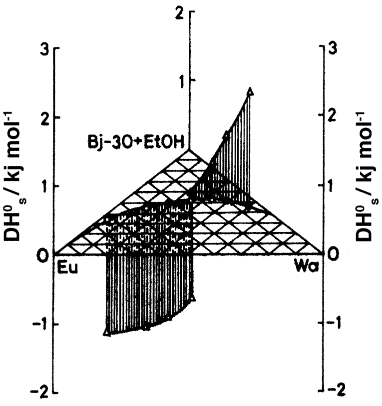

Fig. 9. Enthalpy of dispersion in relation to the triangular phase boundary at 303 K for the system Eu/Bj-30/EtOH/Wa.

4. Conclusions

The water/Brij-30 + EtOH/eucalyptol system forms fair extents of single phase microemulsion with small differences at Brij-30:EtOH weight ratios of 2:1, 1:1 and 1:2. The viscosity of the mixed single phase system thins out with increasing shear rate. At a fixed shear rate viscosity passes through maximum at temperature between 20 and 25 °C; thereafter it shows minimum nearly at 30 °C. The free energy of activation for the viscous flow is not linearly dependent on temperature whereas both the enthalpy and entropy of activation are linearly correlated with temperature. The latter two nicely compensate each other. The enthalpy of solution forming w/o preparations are exothermic whereas the o/w preparations are endothermic. The dimensions of both o/w and w/o dispersions increase with temperature with associated increase in polydispersity.

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