Biological microemulsions: Part III—The formation characteristics and transport properties of saffola-aerosol OT-hexylamine-water system

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The results of formation, phase behaviour and physical properties of biological microemulsions prepared from saffola/AOT/hexylamine/water in presence of different additives, viz. cholesterol, crown ether, urea and brine, are presented. It has been found that the additives and temperature have striking effects; mono-, bi- and triphasic solutions interchanging proportions among themselves. The conduction of microemulsion at different [Water/AOT] ratios (w = 9,10,14,18,20,39 and 45) has shown conspicuous dependence on temperature with a significant degree of percolation, whereas the dependence of viscosity on temperature has shown normal declining trend with temperature. A maximum in viscosity with respect to its variation with amount of water has been observed. The Walden product ($\lambda\eta$) has evidenced noncompensation of ion transport by conduction with the viscosity of the medium. The activation energies evaluated for conduction (ΔE^*_{cond}) and viscosity (ΔE^*_{vis}) are systematic except at [Water/AOT] ratio, w = 20. The additives cholesterol, crown ether and their mixture have shown a decreasing effect on the ΔE^*_{cond} for percolation, whereas ΔE^*_{vis} has increased in their presence. The bicontinuous microemulsion has the prospect for use as liquid membrane.

Microemulsions are low viscous, isotropic, thermodynamically stable mixtures of oil, water, amphiphiles and co-surfactants[1]. Such multicomponent systems containing biologically occurring components have been termed biological microemulsions[2,3], which we have very recently studied using bile salts, proteins and polymers. Their ternary phase diagrams and the effects of different additives and temperature on the phase behaviour and physical properties have been presented. It has been observed that such microemulsions can be fairly stable at 37°C in presence of bile salts, cholesterol, cholesteryl benzoate, gelatin, bovine serum albumin, polyethylene glycol, dextran and polyacrylamide. The microemulsions of such category[4-7], therefore, have the prospect to be used as representative models for natural membranes, where lipid, protein, cholesterol, etc. are the essential structural constituents[8,9]. In recent years, prospective use of microemulsions as liquid membranes for separating and transporting ionic and nonpolar bodies has been demonstrated[10-17].

In our previous studies[2,3], the hydrocarbon heptane was used as the oil, one of the surfactants used was Triton X 100 and butan-1-ol was the co-surfactant. For closer approach to natural system, naturally occurring and biologically compatible oils, surfactants and co-surfactants are to be used. This is not an easy task, for mixing of arbitrarily chosen components may not always yield stable microemulsions. A step forward to this objective has recently been achieved[18], in which the quaternary system studied contained vegetable oil (saffola), Triton X 100, butan-1-ol and water. The system has been found to be fairly stable towards temperature and a number of additives. In this report, we have used the biological detergent Aerosol-OT and hexylamine as the co-surfactant[19]. It may be mentioned that in recent years attempts have been made to prepare microemulsions with triglyceride as oil and phospholipids as the surfactants for the study of the enzyme action on the hydrolysis of glyceride[20]. It will be seen that the present quaternary system has characteristic distinctions which would help in future formulation of microemulsions as media both for kinetic and equilibrium studies.

Experimental

Materials—Sodium di-2-ethyl hexyl sulphosuccinate (AOT), a product of Sigma (USA), was 99% pure and used as such. The oil, saffola containing 73% linoleic acid was a purified product obtained from Bombay Oil Industries Pvt Ltd, Bombay (India). Its estimated acid value was 0.4. Hexylamine (purity 98%) was obtained from E. Merck (Germany) and was used without purification. The additive cholesterol (C) was a purified product[21] of Loba

Chemicals (India) and the crown ether (CE) (18 crown-6) was obtained from Aldrich (USA). Sodium chloride (GR, S. Merck, India) and urea (Excelar grade, BDH, India) were used as received. Doubly-distilled conductivity water of specific conductance 1-2 $\mu S\,cm^{-1}$ at $303^\circ K$ was used for all preparations.

Measurements—The conductance of microemulsions was measured with a conductivity meter of Jenway, England in a cell of cell constant $0.2\,cm^{-1}$.

Viscosity measurements were taken in a calibrated Ostwald viscometer[22,23] assuming Newtonian behaviour of the microemulsions. The flow time for water was 54.6 second at $303^\circ K$. Densities were measured with a calibrated pycnometer[22,23].

Phase changes of microemulsions were studied with a polarising microscope of SICO, India. All the experiments were performed at desired temperatures in a thermostated bath of accuracy $\pm 0.1^\circ C$.

Preparation of microemulsions—The microemulsions were prepared by titrating known quantities (by weight) of mixtures of oil, surfactant and co-surfactant with water added from a microburette up to the point of turbidity determined by observing against cross polarised light. The addition of either extra oil or water yielded biphasic and triphasic preparations. The pseudo ternary phase diagrams were constructed with these data. The surfactant/co-surfactant weight ratio was maintained at 1:1. The phase behavioural experiments were performed at 30, 37 and 40°C. For further details, we refer to our previous publications[2,3,18,22,23]. Several samples of the microemulsions prepared were kept for prolonged time (3-4 weeks) after preparation to check their stability. There was hardly any phase separation or turbidity. The microemulsions got solidified particularly at high oil/water ratio below 20°C and became turbid above 60°C. Therefore, their physico-chemical properties were studied at 1:1 S/CoS ratio at temperatures between 20 and 60°C.

Phase fractions of the microemulsions—The volume fractions of different phases of Winsor I, II and III types microemulsions in presence of the additives brine and urea, and at different temperatures were also determined. In actual experiments, Winsor IV type microemulsions at three different brine or urea or water to oil ratios (viz. 7:1, 1:1, 1:7) and different concentrations of the additives were taken in slender closely graduated stoppered test tubes and were placed in the thermostated bath at $310^\circ K$ to equilibrate. The effect of temperatures on the phase fractions with and without additive was studied in the temperature range $283\text{-}333^\circ K$. Because of the problem of solidification of some samples containing urea at $310^\circ K$, aqueous urea to oil ratios were

taken as 2.8:1, 1:1 and 1:2.8. The samples containing water at water:oil ratio 1:7 solidified all through, and those for combined effects of brine and temperature at the same ratio became turbid at $308^\circ K$ and finally solidified at $313^\circ K$.

After prolonged equilibration, the volumes of the individual phases (mono-, bi-, and tri-) were carefully read. The samples were then thoroughly re-mixed, allowed to re-equilibrate and the volumes of the respective phases were noted again. The average of two readings was recorded. Depending on the compositions and temperature, the extents of the mono-, bi-, and triphasic solutions varied. The results described are the average of duplicate runs evaluated in the above described manner.

Results and Discussions

Phase diagram—The pseudo ternary phase diagrams of the present quaternary system of three temperature 30, 37 and 40°C at S/CoS ratio 1:1 are presented in the phase prism (Fig. 1). All of them
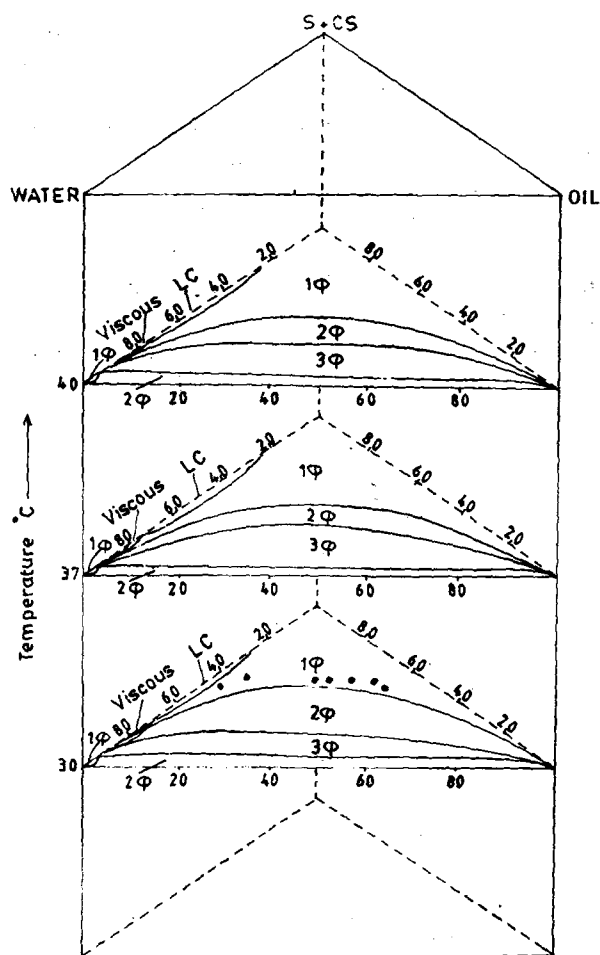

Fig.1 – Phase prism representations of saffola/AOT/hexylamine/water at different temperatures at S/CoS = 1 (w/w) [LC, liquid crystalline]

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have common features of distinct mono-, bi- and tri-phasic zones as well as tiny and narrow, viscous and liquid crystalline (LC) regions respectively towards the water-SCS base line. The bottom 2ϕ zone remains more or less unchanged, whereas the 3ϕ zone expands at 37°C and contracts to a certain extent at 40°C; the 2ϕ zone above it shrinks both at 37°C and 40°C. The top 1ϕ region shows increase with increasing temperature. The tiny 1ϕ zone towards the water corner and the small viscous and narrow LC zones remain practically unaffected by the temperature. With T×100 as the surfactant and butan-1-ol as the co-surfactant, the oil saffola yielded[18] an unusually large 3ϕ zone. There, the 1ϕ (Winsor IV) region increased with temperature, the 3ϕ zone became maximum at 40°C. The viscous and LC zones were absent.

The quaternary system at 1:1 S/CoS ratio at 30°C is also depicted in the tetrahedral representation in Fig. 2. The proportions of the individual phase regions are distinctly understood. Similar diagrams at other two temperatures 37°C and 40°C are not presented to save space. The multiphase formation of quaternary systems of oil, amphiphile, co-surfactant and water is significant. A detailed phase diagramatic representation helps to formulate solutions of different compositions and consistencies. The oil-in-water, water-in-oil as well as bicontinuous[24] (simultaneous dispersions of both oil and water in the medium) dispersions can be prepared and can be used for specific purposes. Depending on the composition, temperature and the additives, the phase forming behaviours of water, oil, amphiphile and co-sur-
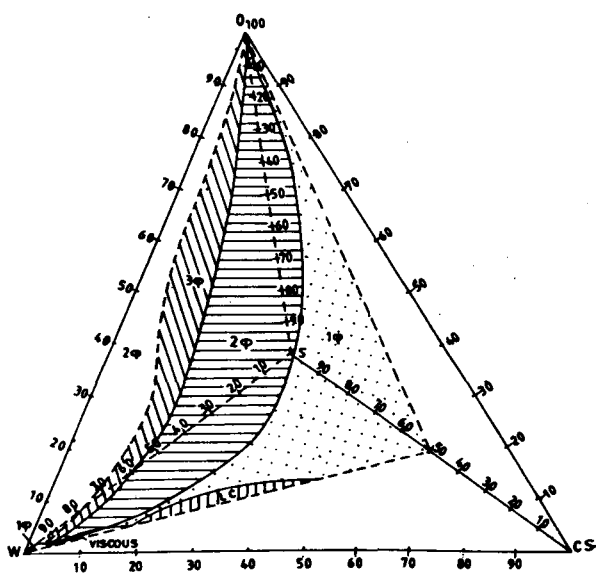
factant can be versatile as well as specific. A detailed study is, therefore, required in this direction.

Conductance—The microemulsion samples corresponding to the points represented by closed circles in the 1ϕ region (Fig. 1) were subjected to conductance measurements at different temperatures. In the seven samples, the [Water/AOT] mole ratio (w) varied from 9 to 45, the compositions covered the o/w to o/w range. It is seen in Fig. 3 that the conductance increases both by the effect of temperature and the water content of the microemulsion. A break in the conductance-temperature plot occurs at 45°C, which sharpens with increase in ω and at $\omega = 45$, the two straight lines of reverse slopes intersect at the transition temperature 45°C. The w/o type microemulsions have been known to
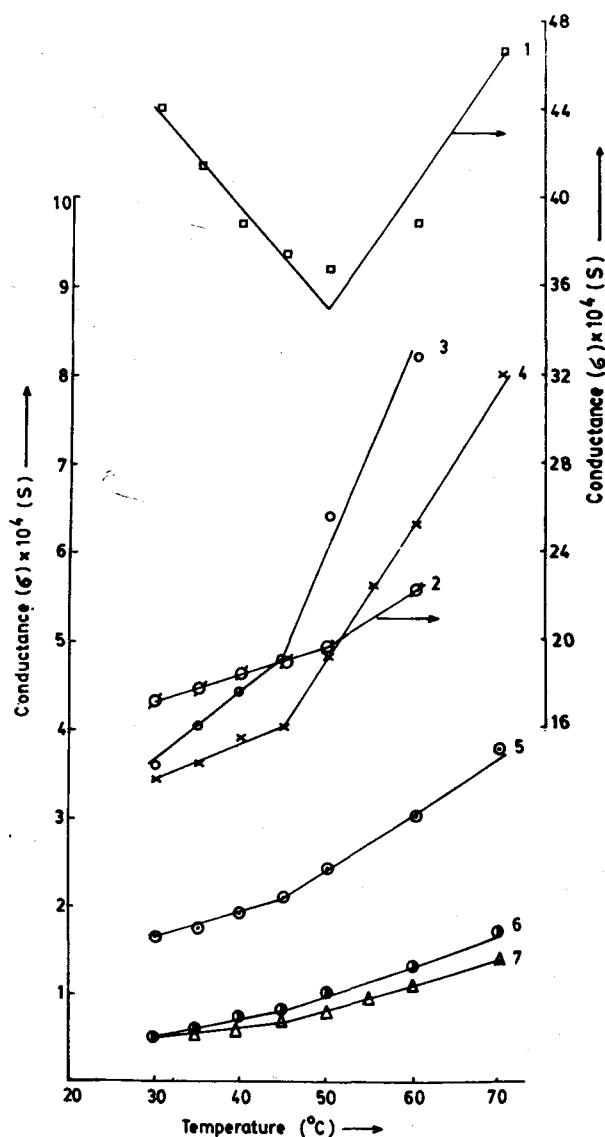

Fig. 2—Tetrahedral representation of saffola/AOT/hexylamine/water at S/CoS = 1 (w/w) at 30°C

Fig. 3—Specific conductance-temperature profile of microemulsion [Curves 1-7, w = 45, 30, 20, 18, 14, 9, 10]

exhibit sudden rise in conductance after a critical temperature, the phenomena is called percolation[23,25-31].

In certain systems, the increment in conductance after the transition may be very large (2-3 orders higher); in the present case the conductance is roughly doubled or trebled. At higher temperature, collision among the dispersed water droplets helps exchange of ions to result in increased conductance. Increased density of the dispersed droplets at higher ω also imparts increment in conductance[32-37]. The decrease in conductance at higher ω, before the percolation transition, tells about changes in the internal structure or arrangement of the system that retards the electrical transport. This kind of retardation has also been observed earlier[18]. The effects of additives on the percolation behaviour of the sample with $\omega = 20$ (curve 3 of Fig. 3) are depicted in Fig. 4. Cholesterol (2% w/w) lowers the transition temperature to 40°C from 45°C, whereas 3% crown ether lowers it to 37°C. A 2% cholesterol and 3% crown ether in combination decrease the threshold by 10°C. It is known that when hydrocarbons are used as oils, cholesterol and its esters make the water/oil interface rigid and increase the transition threshold, whereas crown ether decreases the threshold temperature[37]. The lowering effect of cholesterol is, therefore, not expected. Some unusual conductance and percolation behaviours have

also been observed for the quaternary saffola/T × 100/butan-1-ol/water system in presence of similar additives[18]. The results presented in Fig. 3 show that the rate of conductance increase of the microemulsion systems in the post transition temperature is relatively lower than that without additive.

The variations of log σ with T^{-1} follow linear courses. For samples, with $w = 9$ and 10, the dependence is linear with a single slope and with w equal to 14, 18, 20, 39 and 45, two straight lines with breaks at 39.5, 44.5, 44.5, 49.5, 49.5°C are observed, which are the corresponding percolation thresholds (Fig. 5). The lines 6 and 7, refering to $w = 9$ and 10, respectively, fail to exhibit the transition threshold. The activation energy for conduction, ΔE_{cond}, calculated from the slope is presented
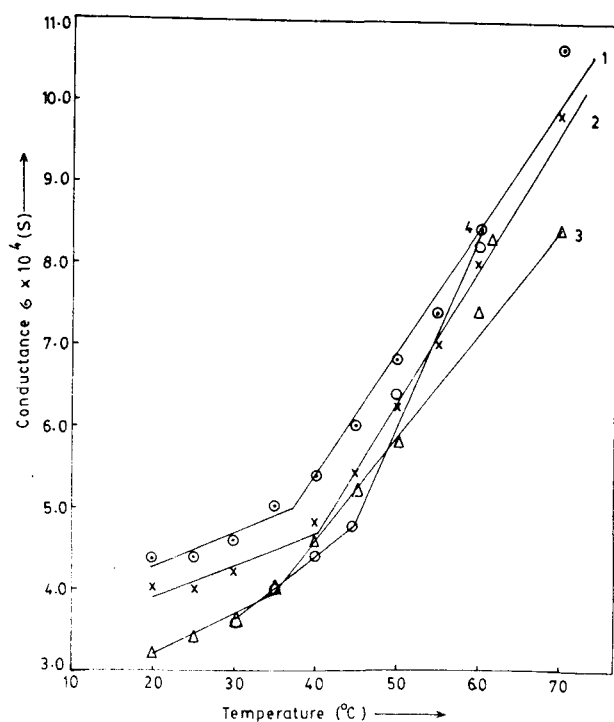

Fig. 4—Specific conductance-temperature profile of microemulsion at $w = 20$ [Curves 1-4, additives (w/v): 3% crown ether, 2% cholesterol, 2% cholesterol + 3% crown ether, 0%]
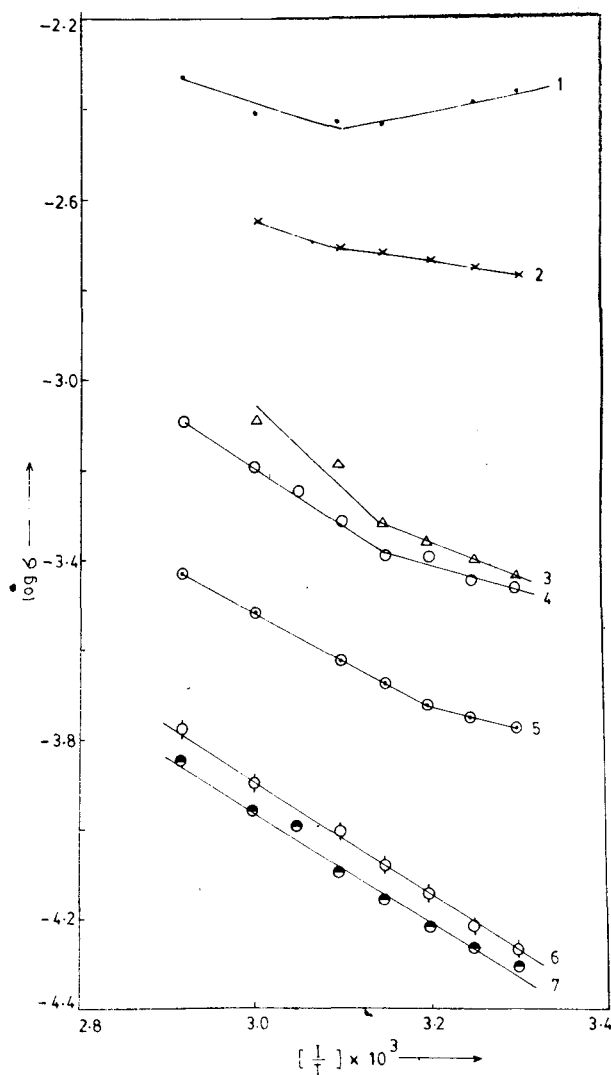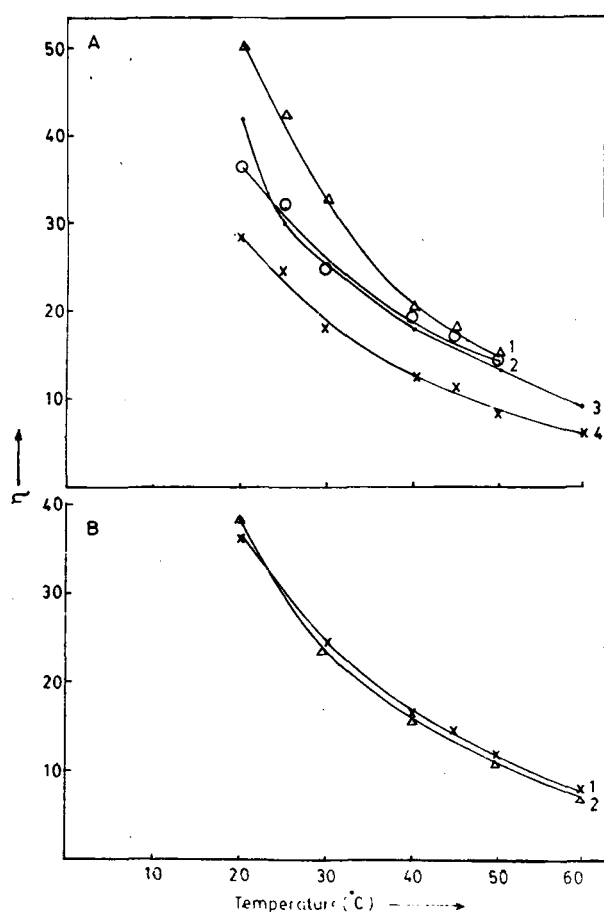

Fig. 5—Logarithm of conductance versus reciprocal of temperature plots for microemulsions [Curves 1-7, $w = 45, 39, 20, 18, 14, 9, 10$]

Table 1 — Activation energies for ionic conduction and viscous flow of saffola/AOT/hexylamine/water microemulsions

Composition S + CoS/Oil/Water	Mol. ratio, $w=[H_2O]/[AOT]$	ΔE^*_{cond} (kJ mol^{-1})		ΔE^*_{vis} (kJ mol^{-1})
		Slope 1	Slope 2	
50/5/45	45	10.78	−8.72	—
55/10/35	39	11.14	5.32	32.53
55/22.5/22.5	20	30.19	15.29	25.17
55/25/20	18	24.73	9.62	35.13
55/30/15	14	20.78	10.02	—
50/40/10	10	22.60	—	—
55/25/10	9	24.91	—	28.56

Fig. 6 — (A): Plots of viscosity of microemulsion as a function of temperature [Curves 1-4. w= 18, 20, 9, 39]

(B): Effect of temperature on the viscosity of microemulsion containing additives at w= 20 [Curves 1-2, 3% crown ether (w/ v), 2% cholesterol (w/v)]

in Table 1. Similar values calculated in presence of additives (curves not shown) are also presented in the table. The activation energies for conduction decrease with increased w, except at W= 20, where it is out of trend and high. With increased level of water, the conductance has increased with decreased energy of activation; the sample 3(w= 20) may have

a different internal structure with a higher value of ΔE_{cond}. At higher level of water, the exchange of counter ions among the colliding water droplets becomes more probable through droplet fusion and separation[38]. The additives cholesterol, crown ether and mixed cholesterol and crown ether have given changed ΔE^*_{cond} values, the mixed additives showing specific influence above the percolation transition, below it their effects are comparable. The ΔE^*_{cond} values range between 6-25 kJ mol^{-1} which are comparable with microemulsions prepared from saffola using T× 100 and butan-1-ol and brine[18]. The values are much lower than those realised with hydrocarbon oils[39].

Viscosity—The dependence of viscosity on temperature using four compositions (w= 9, 18, 20 and 39) is presented in Fig. 6A and the trends in presence of 2% cholesterol and 3% crown ether are shown in Fig. 6B. The dependence is systematic and exponential, no unusual trend in conductance is observed. The activation energy for viscous flow (ΔE^*_{vis}) has been evaluated from the slope of the log η vs T^{-1} plots. The results are presented in Tables 1 and 2. Unlike ΔE^*_{cond}, the ΔE^*_{vis} has a systematic change. The values are on the average same in the presence of the additives. In comparison with our recent study[18] on saffola/T× 100/butan-1-ol/water, these values are 4-6 kJ mol^{-1} higher.

Conductance-viscosity correlation—In the light of electrolyte theory, the two transport phenomena, conductance and viscosity, should have an inverse correlation with the product $\lambda\eta$ = constant (Walden Rule)[40]. In Fig. 7A, the equivalent conductance − wt % water profile is exemplified and the corresponding viscosity − wt % water dependence is depicted in Fig. 7B. A maximum in viscosity has been observed at 20% water, where the conductance appears to take a sharp turn. The viscosity maxima at particular levels of water addition have also been reported[41] in w/o microemulsions with cyclohexane, isooctane and undecane stabilised by AOT. The Walden pro-

Table 2—Activation energies for ionic conduction and viscous flow of saffola/AOT/hexylamine/water microemulsion of composition (55/22.5/22.5 as S + CoS/oil/water) in presence of additives

Additives (%, w/w)	ΔE^*_{cond} (kJ mol^{-1})		ΔE^*_{vis} (kJ mol^{-1})
	Slope 1	Slope 2	
0	30.19	15.29	25.17
3.0, CE	6.45	19.94	30.59
2.0, C	7.31	21.56	31.51
2.0, C + 3.0 CE	13.54	18.29	—

duct $(\lambda\eta)$ vs wt % water is plotted in Fig. 8, where a turn in the course is observed at 22.5% of water, particularly at temperatures below 60°C; at 60°C the course is linear. A close fluctuation is noticed at 20% at the two lower temperatures, 30°C and 40°C. The Walden product is never constant, the regular increasing trend is a consequence of sharp change in conductance, the viscosity decrease cannot compensate for it. This has supported a special internal structural organisation which is reflected on conductance and not much on viscosity[21]. The variation of $\lambda\eta$ with temperature is also revealing, the value
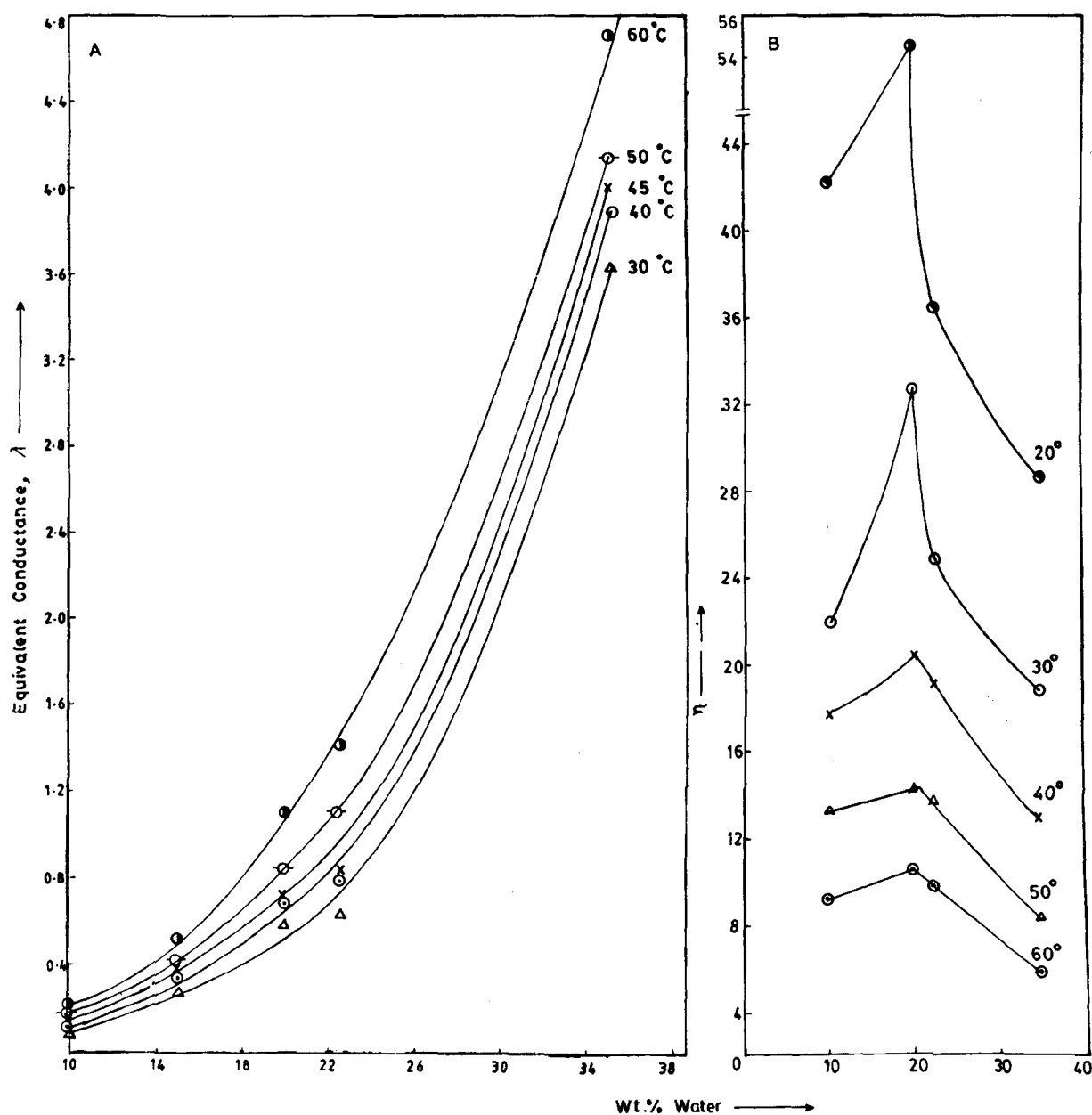

Fig. 7—Dependence of (A) equivalent conductance and (B) viscosity on wt % of water in microemulsion at different temperature
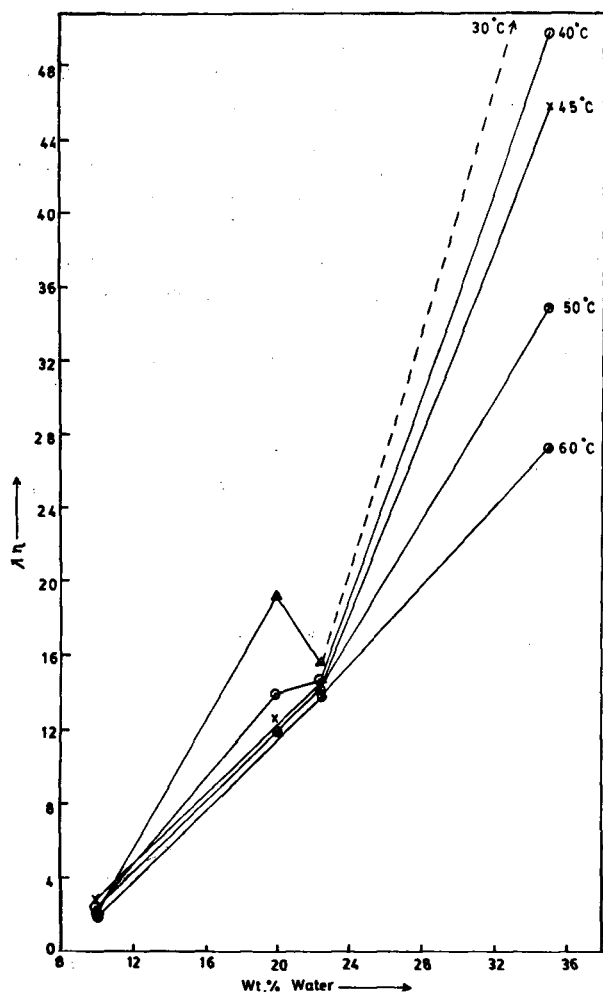
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Fig. 8—Walden product $(\lambda\eta)$ of microemulsion as a function of wt % of water at different temperature

Fig. 9—Walden product $(\lambda\eta)$ of microemulsion at $w = 39, 20, 18$ and 9 as a function of temperature

decreases with temperature (Fig. 9). However, at the lowest value of $w(w=9)$, the compensation is exact, it is shallow at $w=20$. For other values, $w=18$ & 39, the $\lambda\eta$ sharply declines, which is much significant at $w=39$. At higher w, water droplets of sufficient number collide[34-37] with greater frequency leading to large and sharp changes in conductance, which has little scope for response in viscosity. The reciprocal correlation is, therefore, least quantitative. At $\overset{\bullet}{w}=9$, the collision probability among the droplets is low so that a significant change in conductance is not possible, the viscosity and conductance, therefore, can compensate each other. At $w=20$, the presence of 2% cholesterol (C) and 3% crown ether (CE) has also shown sharp declining trends between $\lambda\eta$ and temperature (the graphical presentation is not shown). The above results advocate that membrane conductance may weakly depend on membrane viscosity. The channels which carry the charges (ions) across the barrier are the important
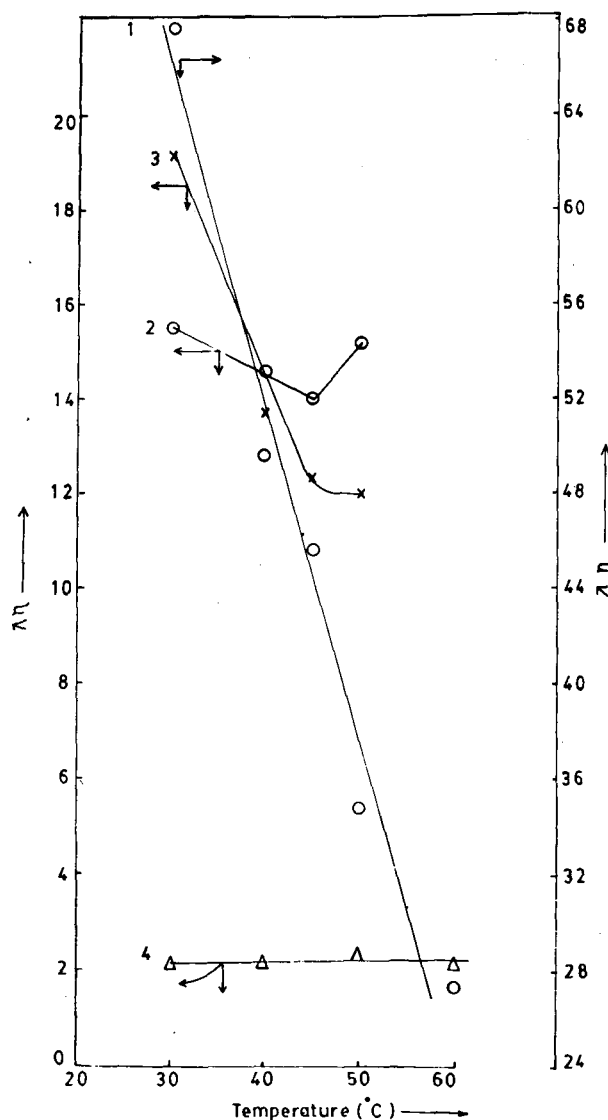
factors. A porous semi-solid body can transport ions favourably through the water filled pores. The conductance can thus be reasonably large, although the semi-solid structure has overall very large viscosity.

Effect of brine—The effect of brine on the phase behaviour of the quaternary system at three compositions, viz. I: 60% S + CoS, 5% oil, 35% brine; II: 60% S + CoS, 20% oil, 20% brine; and III: 60% S + CoS, 35% oil, 5% brine (all wt/wt) at 37°C is presented in Fig. 10. In I, a single phase (Winsor IV) microemulsion results up to 0.2 mol.dm⁻³ brine, thereafter up to 4 mol.dm⁻³ NaCl (the highest brine concentration) the system is biphasic, the upper phase is w/o type. Winsor I and the lower phase is a micellar solution in brine. Increase of oil in the qua-
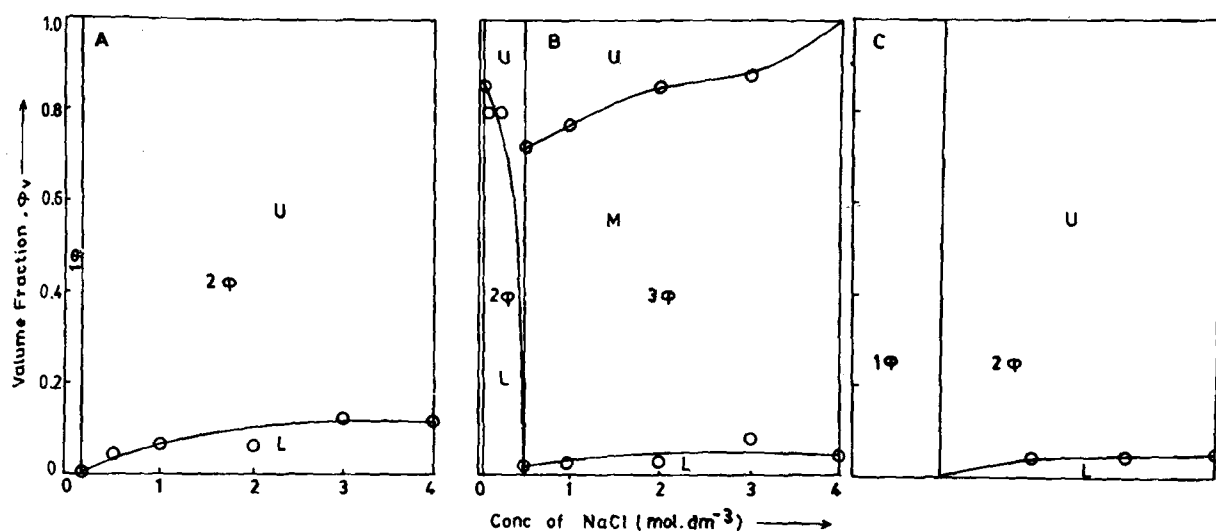
Fig. 10—Brine affected phase volume fractions of ternary saffola/AOT/hexylamine/water system at 37°C [Curve A, S + CoS/oil/brine = 60/5/35 (w/w); B, S + CoS/oil/brine = 60/20/20 (w/w); C, S + CoS/oil/brine = 60/35/5 (w/w)].

ternary system makes a radical change in the phase behaviour. In sample II, up to 0.5 mol.dm^{-3} brine, the system is biphasic. The decrease in the lower phase is compensated by the increase in the upper phase and, after 0.5 mol.dm^{-3}, there appears three phases; the lower one is a micellar solution of AOT in brine, the upper one is the solution of the cosurfactant hexylamine in oil and the middle phase is bicontinuous microemulsion phase which is very broad. The lower phase remains independent of brine concentration, the bicontinuous microemulsion phase (Winsor III) increases at the expense of the upper phase. In sample III, the change is again dramatic. The system is monophasic microemulsion (Winsor IV) up to 1 mol.dm^{-3} brine, thereafter the lower phase is narrow all through and the upper microemulsion phase (Winsor I) is very broad with almost unchanged proportion. The versatile nature of the system with respect to brine is envisaged. The effect of temperature on samples I & II in absence of brine is depicted in Fig. 11. The first sample remains monophasic up to 30°C, between 30°-40°C the mixture is triphasic, the middle and upper phases compensate between them; the fraction of the lower phase remains unchanged. Between 40°-60°C (60°C is the maximum temperature studied), the system turns into a biphasic solution with 95% of the volume to the upper microemulsion phase. The sample III of the composition given above becomes pasty solid with high consistency above 25°C and remains so up to 60°C.

In presence of 0.85 mol.dm^{-3} NaCl, the samples I & II have also shown distinct phase behaviour with respect to temperature (Fig. 12). The sample II is
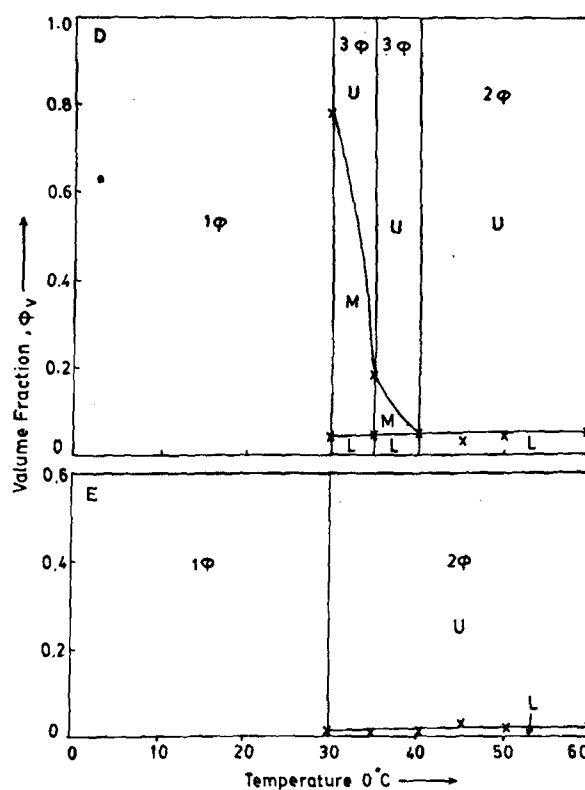

Fig. 11—Effect of temperature on the phase volume fractions of ternary saffola/AOT/hexylamine/water system. [Curve D, S + CoS/oil/water = 60/5/35 (wt/wt); E, S + CoS/oil/water = 60/20/20 (wt/wt)]

monophasic up to 30°C, it is biphasic between 30°C and 40°C, and triphasic above 40°C up to 60°C. It is radically different from the phase behaviour without NaCl. The sample I with 0.85 mol.dm^{-3} NaCl is again very different from that without NaCl. The

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former has no three phase region which is prominent between 30°-40°C in the latter. Here again the sample III has been distinctly clear up to 30°C and
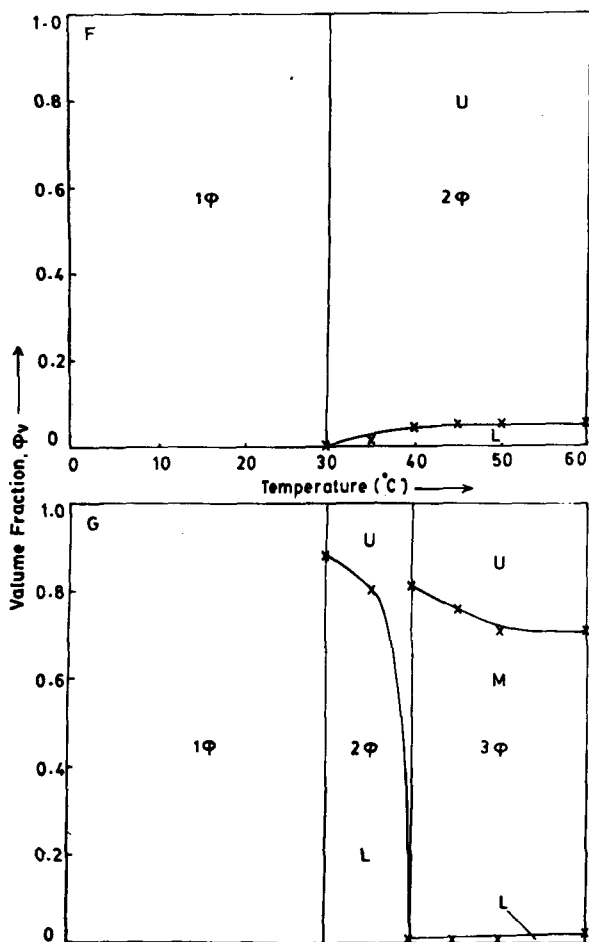

Fig. 12—Effect of temperature on the phase volume fractions of ternary saffola/AOT/hexylamine/water system at two different brine compositions [Curve F, S + CoS/oil/water = 60/5/35 (wt/wt); G, S + CoS/oil/water = 60/20/20 (wt/wt)]

then turbid up to 35°C. From 35°C, the sample has shown a tendency of solidification which is distinct at 40°C, and this property is retained up to 60°C.

Effect of urea—Effects of urea on sample IV (5% S + CS, 25% oil, 70% urea), sample V (5% S + CS, 47.5% oil, 47.5% urea) and sample VI (5% S + CS, 70% oil, and 25% urea) all w/w at 37°C, are presented in Fig. 13. Up to 8 mol.dm^{-3} aqueous urea, the quaternary system is although biphasic, approximately 70% of the mixture constitutes the lower phase, beyond 6 mol.dm^{-3} the volume of it is 10% less. The sample V is all through triphasic, on the average 30% of the total volume constitutes the middle bicontinuous phase. The nature of sample VI is radically different from IV & V. Up to 6 mol.dm^{-3}, three phases coexist; thereafter, the sample is biphasic. A striking constancy in the fraction of upper phase has been observed, it is 75% of the total. In the three phase region, the lower phase declines with urea with a concomitant rise in the middle phase.

Urea can form channel compounds[42] with hydrocarbons. We have observed that urea can form increased single phase microemulsion at low percentage of S + CS, when heptane is the oil and T × 100 and butan-1-ol are the surfactant and cosurfactant respectively[2]. In case of saffola, low concentration of S + CS (AOT + HA) can form appreciable amount of microemulsion, it can also significantly affect the phase behaviour. Since urea can form channels in the microemulsion, these channels filled with the oil can be potential routes for transport of nonpolar substrates. The use of urea in microemulsion could, therefore, be useful in the study of their membrane behaviours.
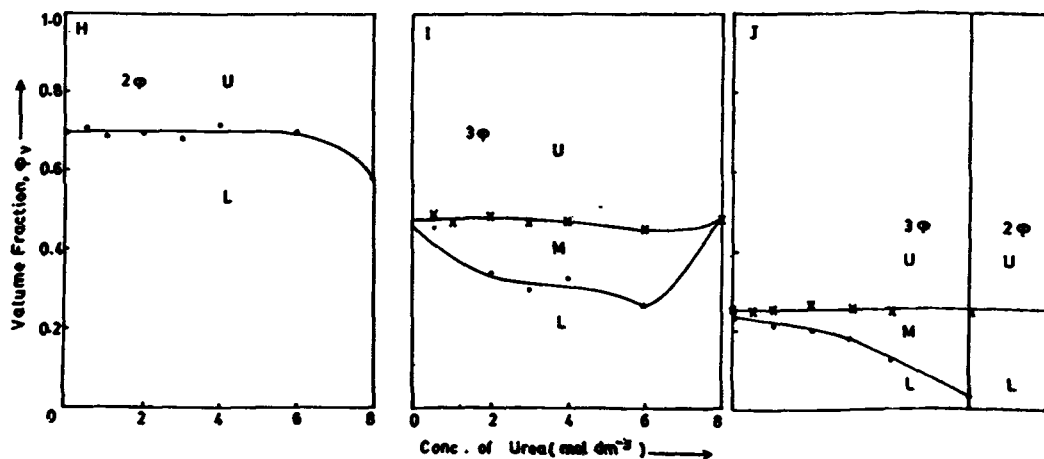

Fig. 13—Effect of urea on the phase volume fractions of ternary saffola/AOT/hexylamine/water system at 37°C [Curve H, S + CoS/oil/water = 5/25/70 (wt/wt); I, S + CoS/oil/water = 5/47.5/47.5 (wt/wt); J, S + CoS/oil/water = 5/70/25 (wt/wt)]

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