

Studies on Molar Volume and Rheology of Terbium Soaps in a Benzene-DMF Mixture

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Summary. Molar volume (\bar{V}), apparent molar volume (ϕ_v), and fluidity (ψ) of terbium soaps in benzene-DMF (7:3 v/v) were evaluated at constant temperature from density and viscosity measurements. The results were used to determine the critical micelle concentration (CMC), soap-solvent and soap-soap interactions, and the effect of the chain length of soap molecules on various parameters. The molar volume and viscosity results are discussed in terms of known relations.

Keywords. Terbium soaps; Molar volume; Critical micelle concentration; Soap-solvent interaction; Rheological parameters.

Untersuchungen zum Molvolumen und zur Rheologie von Terbiumseifen in Benzol-DMF

Zusammenfassung. Molvolumen (\bar{V}), scheinbares Molvolumen (Φ_v) und Fluidität (Ψ) von Terbiumseifen in einer Mischung aus Benzol und DMF (7:3 v/v) wurden bei konstanter Temperatur aus Dichte- und Viskositätsmessungen ermittelt. Aus den Ergebnissen wurden die kritische Micellenkonzentration (CMC), Seifen-Lösungsmittel- und Seifen-Seifen-Wechselwirkungen sowie der Effekt der Kettenlänge der Seifenmoleküle auf verschiedene Parameter bestimmt. Die Resultate bezüglich Molvolumen und Viskosität werden anhand bekannter Beziehungen diskutiert.

Introduction

The most striking feature of metallic soaps is their increasing importance in industry. Although a great amount of work has been reported on alkali, alkaline, and transition metal soaps, only few studies on rare earth metal soaps have been performed [1–14] inspite of their broad use. The technological applications of these soaps are mostly based on empirical know-how, and the selection of a soap depends largely on economic factors.

A metal soap in dilute solution is largely present as metal cations and fatty acid anions, and many physical properties of soap solutions exhibit characteristic transitions at minute changes of concentration. This transitions are generally related to the formation of aggregates arising from the intrinsic amphiphilic nature of soap molecules. The transition region has been used to determine the critical micellar concentration (CMC), above which multimolecular aggregates (micelles) are formed. The forces that hold together amphiphilic molecules in micelles arise from weak *Van der Waals*, hydrophobic, hydrogen bonding, and electrostatic interactions.

Measurements of molar volume and rheological parameters have been used to determine the CMC of metal soaps [15–17] in non-aqueous media. The apparent and partial molar volume data for electrolytes [18] and non-electrolytes [19] have been employed to obtain information regarding solute-solute, solute-solvent, and solvent-solvent interactions in soap solutions.

In the present work, attempts have been made to compute molar volume, apparent molar volume, and rheological parameters of terbium soaps (myristate, palmitate, and stearate) in a benzene-DMF mixture (7:3 v/v) at constant temperature ($40 \pm 0.05^\circ\text{C}$). The data provide useful information about CMC, ion-solvent, and ion-ion interactions and about the polydispersity of soap molecules in solutions.

Results and Discussion

Molar Volume

Molar volume (\bar{V} , $\text{dm}^3 \cdot \text{mol}^{-1}$) and apparent molar volume (ϕ_v , $\text{dm}^3 \cdot \text{mol}^{-1}$) [20] have been evaluated from Eqs. 1 and 2.

$$\bar{V} = M/\rho \quad (1)$$

$$\phi_v = \frac{10^3}{c \cdot \rho \cdot \rho_0} (\rho_0 - \rho) + \frac{M}{\rho} \quad (2)$$

M , ρ ($\text{kg} \cdot \text{m}^{-3}$), ρ_0 ($\text{kg} \cdot \text{m}^{-3}$), and c ($\text{mol} \cdot \text{dm}^{-3}$) represent molecular weight of soap, density of solution, density of solvent, and concentration of soap solution, respectively.

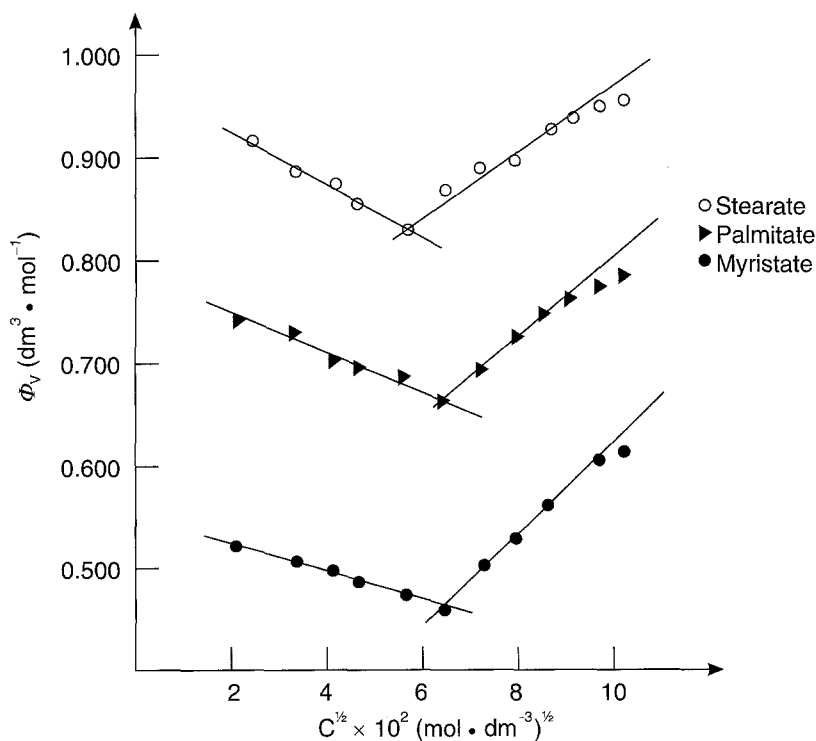


Fig. 1. Apparent molar volume (ϕ_v) vs. concentration ($c^{1/2}$)

The molar volume of the solutions of terbium soaps (myristate, palmitate, and stearate) in benzene-DMF (7:3 v/v) at $40 \pm 0.05^\circ\text{C}$ decreases with increasing soap concentration (Table 1). This plots of molar volume *vs.* soap concentration are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC of the soap (myristate: 0.0045 M; palmitate: 0.0040 M; stearate: 0.0033 M). The values of CMC are in agreement with those obtained from ultrasonic measurements [21] of soap solutions (Table 2).

The values of apparent molar volume first increase and then decrease with increasing soap concentration (Fig. 1). The limiting apparent molar volumes have been obtained by extrapolating the plots of ϕ_v *vs.* $c^{1/2}$ for dilute soap solutions according to *Masson's* equation [22]:

$$\phi_v = \phi_v^0 + S_v c^{1/2} \quad (3)$$

The values of limiting apparent molar volume (ϕ_v^0 , $\text{dm}^3 \cdot \text{mol}^{-1}$) and constant S_v ($\text{dm}^{9/2} \cdot \text{mol}^{-3/2}$) are a measure of soap-soap and soap-solvent interactions, respectively (Table 2). The positive values of S_v suggest high soap-solvent interactions in these solutions. The values of ϕ_v^0 decrease with increasing chain length of soap molecules (Table 2). The results are in agreement with the results reported by *Masson* [22] for electrolytic solutions.

Rheology

Viscosity (η , Pascal·s) and fluidity (ψ , $\text{Pascal}^{-1} \cdot \text{s}^{-1}$) are considered to be important rheological parameters. The viscosity of the soap solutions in benzene-DMF increases with increasing concentration and chain length of soap molecules (Table 1). This may be due to the increasing tendency of the soap molecules to form aggregates with increasing concentration and chain length. The plots of viscosity *vs.* soap concentration (Fig. 2) are characterized by a break at a definite soap concentration which corresponds to the CMC of the soap (myristate: 0.0045 M; palmitate: 0.0039 M; stearate: 0.0034 M). The increase in viscosity above CMC may be attributed to the fact that the aggregation of the soap molecules boosts up the electrokinetic forces, causing more intake of the solvent and resulting in increasing viscosity of the system.

The results of viscosity measurements can be explained in terms of equations proposed by *Einstein* [23], *Vand* [24], *Moulik* [25], and *Jones-Dole* [26] (η_0 : viscosity of solvent; η_{sp} : specific viscosity). M and K are *Moulik's* constants, and A and B refer to *Jones-Dole's* constants.

$$\text{Einstein:} \quad \eta_{\text{sp}} = 2.5\bar{V}c$$

$$\text{Vand:} \quad 1/c = \left(\frac{0.921}{\bar{V}}\right)^{-1} \cdot \frac{1}{\log(\eta/\eta_0)} + \theta\bar{V}$$

$$\text{Moulik:} \quad (\eta/\eta_0)^2 = M + Kc^2$$

$$\text{Jones-Dole:} \quad (\eta_{\text{sp}}/\sqrt{c}) = A + B\sqrt{c}$$

The plots of η_{sp} *vs.* c are linear below CMC with intercepts almost equal to zero which shows that *Einstein's* equation is applicable to the soap solutions and there is no appreciable aggregation below CMC. The molar volumes of the soaps have been

Table 1. Molar volume and viscosity of terbium soaps (solvent composition: benzene-DMF, 7:3 (v/v))

$c \times 10^3$ (mol·dm ⁻³)	$\bar{V} \times 10^{-3}$ (dm ³ ·mol ⁻¹)	η (Pascal·s)	$\eta_{sp} \times 10^3$	η_{sp}/\sqrt{c}	$(\eta/\eta_0)^2$	$1/\log \eta/\eta_0$	$-\phi_v \times 10^3$ (dm ³ ·mol ⁻¹)
Myristate							
0.5	0.9324	0.5514	2.00	0.80	1.003	—	530.16
1.0	0.9322	0.5526	4.00	1.27	1.008	577.25	515.21
1.5	0.9320	0.5538	6.30	1.62	1.012	373.90	500.03
2.0	0.9317	0.5549	8.18	1.83	1.016	282.78	494.67
3.0	0.9313	0.5570	12.00	2.19	1.024	193.13	481.16
4.0	0.9309	0.5594	16.35	2.59	1.033	141.96	471.91
5.0	0.9302	0.5627	22.35	3.16	1.045	104.18	510.77
6.0	0.9296	0.5661	28.52	3.68	1.058	81.87	536.08
7.0	0.9289	0.5702	35.97	4.30	1.073	65.15	571.05
8.0	0.9283	0.5774	43.60	4.78	1.089	53.95	582.94
9.0	0.9373	0.5788	51.60	5.44	1.106	45.77	616.82
10.0	0.9268	0.5822	57.78	5.78	1.119	40.99	621.81
Palmitate							
0.5	1.0255	0.5520	2.80	1.11	1.005	—	766.19
1.0	1.0252	0.5532	5.09	1.61	1.010	453.71	740.38
1.5	1.0249	0.5546	8.00	2.06	1.015	302.89	722.79
2.0	1.0245	0.5566	10.17	2.28	1.020	227.46	711.22
3.0	1.0238	0.5588	15.26	2.78	1.031	152.02	703.23
4.0	1.0232	0.5614	20.00	3.16	1.040	116.36	679.31
5.0	1.0223	0.5656	27.62	3.19	1.056	84.52	710.64
6.0	1.0214	0.5697	35.07	4.53	1.071	66.81	740.24
7.0	1.0204	0.5740	42.88	5.72	1.088	54.89	761.40
8.0	1.0196	0.5788	51.60	5.77	1.106	45.77	777.26
9.0	1.0187	0.5830	59.23	6.24	1.122	40.02	789.60
10.0	1.0171	0.5869	66.32	6.63	1.137	35.86	799.42
Stearate							
0.5	1.1184	0.5530	4.00	1.92	1.009	—	941.35
1.0	1.1180	0.5545	7.45	2.35	1.015	310.25	910.62
1.5	1.1178	0.5560	9.41	2.70	1.020	227.46	887.61
2.0	1.1172	0.5579	13.63	3.04	1.029	170.13	883.30
3.0	1.1163	0.5605	18.35	3.35	1.037	124.62	851.28
4.0	1.1152	0.5647	25.98	4.11	1.053	89.77	888.30
5.0	1.1141	0.5697	35.07	4.96	1.071	66.81	910.50
6.0	1.1132	0.5740	42.88	5.53	1.088	54.84	918.30
7.0	1.1118	0.5790	51.96	6.21	1.107	45.85	931.79
8.0	1.1109	0.5842	61.41	6.87	1.127	38.63	959.93
9.0	1.1100	0.5880	68.31	7.20	1.141	34.89	977.64
10.0	1.0188	0.5924	76.31	7.63	1.158	31.22	982.71

evaluated from the slope of *Einstein's* plot. The values of molar volume and interaction coefficient (θ) have also been evaluated using *Vand's* plots ($1/c$ vs. $1/\log \eta/\eta_0$). The values of molar volume obtained from the slopes of *Einstein's* and *Vand's* plots were found to be in agreement (Table 2). The values of the interaction coefficient decreases with increasing in chain length of soap molecules.

Table 2. Viscometric measurements of terbium soaps

Soap	\bar{V} (dm ³ ·mol ⁻¹)	CMC (mol·dm ⁻³)		Ultrasonic velocity, v (m·s ⁻¹)	$-\phi_v^0$ (dm ³ ·mol ⁻¹)	S_v (dm ^{9/2} ·mol ^{-3/2})	η_0 (Pascal·s)	\bar{V} (dm ³ ·mol ⁻¹)		θ
	<i>vs.</i> c (mol·dm ⁻³)	η (Pascal·s)	<i>vs.</i> c (mol·dm ⁻³)					<i>Einstein</i>	<i>Vand</i>	
Myristate	0.0045	0.0045	0.0045		0.549	1.27	0.5504	1.60	1.87	16.0
Palmitate	0.0040	0.0039	0.0040		0.780	1.77	0.5508	2.00	2.17	13.8
Stearate	0.0033	0.0034	0.0034		0.960	2.50	0.5504	2.41	2.64	11.3
Soap	M	<i>Moulik's constants</i>		<i>Jones-Dole's constants</i>						
		K	A	B	$\{\eta\}$					
		(mol ⁻² ·dm ⁶)	(dm ^{3/2} ·mol ^{-1/2})	(dm ³ ·mol ⁻¹)	(dm ³ ·mol ⁻¹)					
Myristate	1.002	24.00	0.01	3.97	4.0					
Palmitate	1.010	26.25	0.05	4.04	5.1					
Stearate	1.012	27.50	0.09	4.31	7.5					

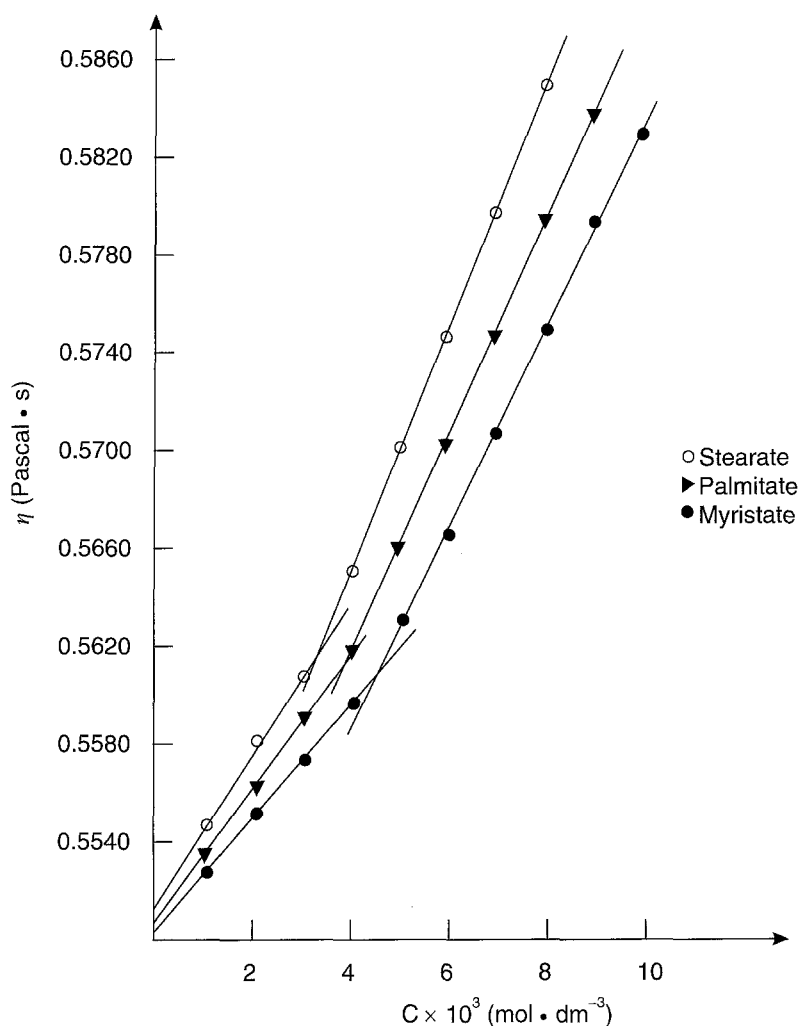


Fig. 2. Viscosity *vs.* concentration

The values obtained for *Moulik's* constants M and K ($\text{mol}^{-2} \text{dm}^6$) from the plots of $(\eta/\eta_0)^2$ *vs.* c^2 show that the values of K are much higher than those of M (Table 2). The values of M were found to be almost independent of the chain length of the soap, whereas the values of K showed an increase with increasing chain length of soap molecules (Table 2).

The constants A ($\text{dm}^{3/2} \cdot \text{mol}^{-1/2}$) and B ($\text{dm}^3 \text{mol}^{-1}$) of *Jones-Dole's* equation have been evaluated from intercept and slope of the plots of η_{sp}/\sqrt{c} *vs.* $c^{1/2}$. The values of B (soap-solvent interaction) were found to be greater than those of A (soap-soap interaction), again confirming the predominance of soap-solvent interactions in dilute solutions. The values of constants A and B were found to increase with increasing chain length of the fatty acid constituents of the soap molecules.

The values of intrinsic viscosity ($\{\eta\}$, $\text{mol}^{-1} \cdot \text{dm}^3$) for terbium soaps obtained from the plots of η_{sp}/c *vs.* c show an increase with increasing in chain length of

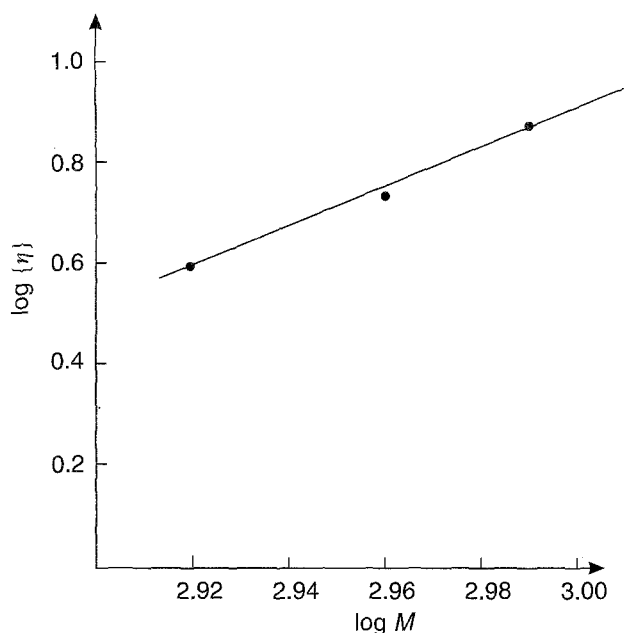


Fig. 3. $\log \{\eta\}$ vs. $\log M$

soap molecules (Table 2). The values of proportionality factor (K) and shape factor (α) of *Mark-Houwink-Staudinger's* equation have been evaluated from the intercept and slope of the plot of $\log \{\eta\}$ vs. $\log M$ for terbium soaps (Fig. 3). The value of the shape factor (3.5) suggests that the soap molecules behave like stiff rods. The values of the proportionality factor for terbium soaps are found to be equal to 0.62.

The plots of fluidity vs. concentration show that the fluidity decreases with increasing soap concentration due to the increasing tendency of the formation of micelles. In dilute solutions of terbium soaps, the cations and anions are so far apart that they have but insignificant interactions; as the concentration increases, the anions tend to congregate in the vicinity of cations and *vice versa*.

Experimental

All chemicals used were of BDH/AR grade. The soaps (myristate, palmitate, and stearate of terbium) were prepared by direct metathesis of the corresponding potassium soap with the required amount of aqueous solution of terbium nitrate at 50–55 °C under vigorous stirring. The precipitated soaps were washed with water and acetone to remove excess of metal ions and unreacted fatty acids and were recrystallized from benzene-methanol. The purity of soaps was checked by determining their melting points and by elemental analysis; the results were found to be in agreement with the theoretically calculated values. The absence of hydroxy groups was confirmed by the absence of any peak in the region of 3000–3500 cm^{-1} in IR spectra of the soaps. The reproducibility was checked by preparing the soaps twice under similar conditions.

Solutions of soaps were prepared by dissolving a known amount of soap in a mixture of benzene-DMF (7:3 v/v) as these soaps show a solubility maximum in this solvent mixture. The solutions were kept in a thermostat at the desired temperature for 2 h.

A pyrex glass dilatometer with a 15 cm^3 reservoir was used to determine the molar volume of solutions at constant temperature (40 ± 0.05 °C). The dilatometer was calibrated with water and

benzene. The reproducibility of the results was $\pm 0.0002 \text{ g}\cdot\text{cm}^{-3}$. The viscosity of terbium soap solutions were measured using *Ostwald's* viscometer at $40 \pm 0.05^\circ\text{C}$.

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References

- [1] Mehrotra RC (1965) *Wiss Z Friedrich-Schiller Univ Jena Math Naturwiss Reihe* **14**: 171
- [2] Chatfield HW (1936) *Paint Manuf* **6**: 112
- [3] Skrylev LD, Sazonna VF, Kornelli ME, Shumitina NA (1978) *Khim Khim Technol* **21**: 491
- [4] Skellon JH, Andrews KE (1955) *J Appl Chem (Lond)* **5**: 245
- [5] Misra SN, Misra TN, Mehrotra RC (1963) *J Inorg Nucl Chem* **25**: 195
- [6] Skellon JH, Spence JW (1953) *J Appl Chem (Lond)* **3**: 10
- [7] Bhandari AM, Dubey S, Kapoor RN (1970) *J Am Oil Chem Soc* **4**: 47
- [8] Solanki AK, Bhandari AM (1981) *Tenside Detergents* **18**: 34
- [9] Varma RP, Jindal R (1983) *Tenside Detergents* **20**: 193
- [10] Mehrotra KN, Gahlaut AS, Meera Sharma (1986) *J Am Oil Chem Soc* **63**: 1571
- [11] Mehrotra KN, Gahlaut AS, Meera Sharma (1987) *J Colloid Interface Sci* **120**: 110
- [12] Mehrotra KN, Upadhyaya SK (1988) *J Chem Eng Data* **33**: 468
- [13] Mehrotra KN, Upadhyaya SK (1991) *Pol J Chem* **65**: 1035
- [14] Mehrotra KN, Somya Gupta (1993) *Acoust Lett* **16**: 266
- [15] Mehrotra KN, Meera Sharma, Gahlaut AS (1989) *Recl Trav Chim Pays-Bas* **108**: 256
- [16] Mehrotra KN, Kirti Tandon, Rawat MK (1992) *J Indian Chem Soc* **69**: 193
- [17] Mehrotra KN, Shukla RK, Mithlesh Chauhan (1990) *J Appl Poly Sci* **39**: 1745
- [18] Millers FJ (1971) *Chem Rev* **147**: 71
- [19] Franks F, Ives DJG (1966) *Quart Rev* **1**: 20
- [20] Bouguerra S, Letellier P (1982) *J Chem Phys* **79**: 845
- [21] Mehrotra KN, Sharma N (1995) *Acoust Lett* (in press)
- [22] Masson DO (1929) *Phil Mag* **8**: 218
- [23] Einstein A. *Ann Physik* **19** (1906): 289; **34** (1911): 591
- [24] Vand V (1948) *J Phys Colloid Chem* **52**: 277
- [25] Moulik SP (1968) *J Phys Chem* **72**: 4682
- [26] Jones G, Dole M (1929) *J Am Chem Soc* **51**: 2950

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