Acoustical Parameters and Apparent Molar Volume of Lithium Soaps in Methanol

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Ultrasonic velocity and density measurements of lithium soaps (abietate, oleate and myristate) were measured in methanol at different frequencies (1-5 MHz) and under different conditions to determine critical micelle concentration and various acoustical parameters for the soap solutions. The evaluated parameters of ultrasonic velocity and the density data suggest a significant solute-solvent interaction in dilute solution and micellar aggregation at higher concentration.

Key Words: Soaps, CMC, Ultrasonic velocity, Density, Lithium soaps, Myristate, Oleate, Rosin soap, Surfactants.

INTRODUCTION

The uses of lithium soaps have already been discussed[1]. Ultrasonic investigations have been used to study ion-solvent interaction[2]. These studies may also be applied to soap solutions because the ultrasonic velocity depends on many factors like intermolecular force[3], non-ideality in free length[4] and interactions due to ion association. The kinetics of micellization have been studied[5] by using ultrasonic relaxation studies in surfactant solutions at concentrations greater than the CMC (critical micelle concentration).
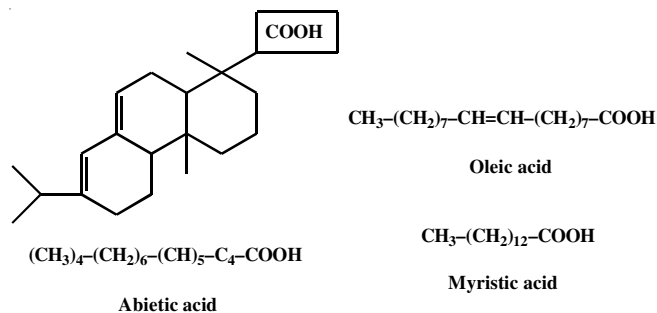
The present study is a continuation of previous work with lithium soaps[1]. In this paper, the ultrasonic velocity and density of lithium soaps (abietate, oleate and myristate) have been measured in methanol at different temperature to calculate several acoustical parameters as well as CMC's for soaps of different structures to examine micellar aggregation and soap-solvent interactions.

EXPERIMENTAL

Lithium carbonate, oleic acid and myristic acid and methanol were of AR grade. Abietic acid was obtained from rosin acid by using the method discussed in a previous paper[1].

Preparation of soaps: Lithium soaps of abietic acid ($C_{19}H_{29}COOH$), oleic acid ($C_{17}H_{35}COOH$) and myristic acid ($C_{13}H_{27}COOH$) were prepared[6] by neutralizing equivalent amounts of fatty and rosin acids with lithium carbonate, respectively. The soaps were purified by re-crystallization in methanol and then dried in an oven at 105 ℃ for 1 h. The

soaps were chosen to study the comparison in properties due to descending number of carbon atoms and also due to different type of structures of soaps as shown below:

$CH_3–(CH_2)_7–CH=CH–(CH_2)_7–COOH$

Oleic acid

$CH_3–(CH_2)_{12}–COOH$

Myristic acid

$(CH_3)_4–(CH_2)_6–(CH)_5–C_4–COOH$

Abietic acid

Preparation of solutions: A calculated amount of the soap was weighed in a standard flask. The desired solution was produced by adding the required amount of methanol.

Densities were measured at different temperatures using a dilatometer made of pyrex glass having a reservoir volume of 20 cm³. The measuring section was a precisely bored graduated capillary. The uncertainty in the density measurements is ± 0.1 Kg/m³. Ultrasonic velocities of soap solutions were measured with a multi-frequency single-crystal ultrasonic interferometer (Mittal Enterprises, New Delhi, India) with a working range of 1-5 MHz. Water from a thermostat maintained at the desired temperature and controlled to ± 0.05 ℃ was passed through the jacket to the cell before measurements were made. The uncertainty in the measured ultrasonic velocity is estimated to be ± 0.05 ms⁻¹.

RESULTS AND DISCUSSION

The plots of ultrasonic velocity, c (m/s), *versus* soap concentration, C (mol/dm³) (Fig. 1) show a critical micelle concentration (CMC) of 0.010 M for abietate soap, 0.015 M for oleate and 0.010 M for myristate. These values are similar to those observed in aqueous solutions[1] except for myristate, which is not sufficiently soluble in water. These values are the same as measured from density, ρ (g cm⁻³) *versus* concentration, C (mol dm⁻³) plots (Fig. 2). The density of Li-soaps in methanol increase with increase of concentration but decrease with increase in temperature. The critical micelle concentration is independent of temperature.
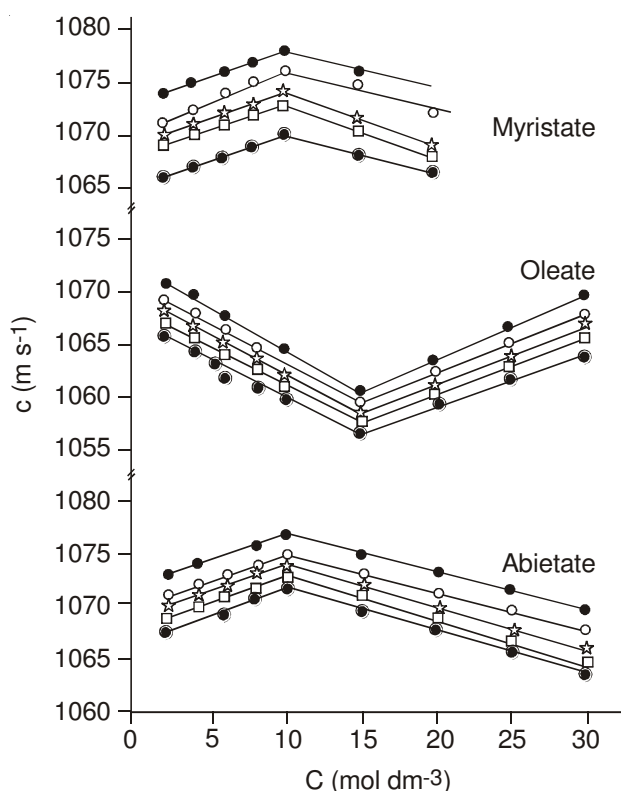

Fig. 1. Plots of ultrasonic velocity, c (m/s) *versus* concentration, C mol dm⁻³ of lithium soaps in methanol at multi-frequency at 35 ºC. ● 1 MHz, ○ 2 MHz, ☆ 3 MHz, □ 4 MHz, ◉ 5 MHz
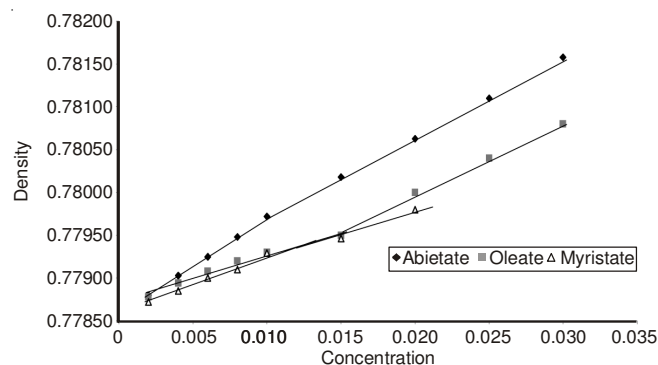

Fig. 2. Plots of density (g dm⁻³) *verses* concentration C (mol dm⁻³) in methanol at 35 ºC

It is observed that the values of ultrasonic velocities shown in Fig. 1 are lower than the values in water by 30 % approxi-

mately. The ultrasonic velocities decrease with the increase in frequency of ultrasonic waves in methanol. The ultrasonic velocities of soap solutions for the different soaps in methanol are in the order: abietate > myristate > oleate. The different shape of oleate soap curves in Fig. 1 can be explain due to the different types of packing of soap molecules in solution which supported by adiabatic compressibility values for oleate.

Through use of the values of ultrasonic velocity the adiabatic compressibility, β, of solutions are calculated by using the relation

$$\beta = \frac{1}{c^2 \rho} \tag{1}$$

where ρ = density of the solution. The variation of ultrasonic velocity with concentration (dc/dC) therefore depends on the derivative with respect to concentration of density and adiabatic compressibility:

$$\frac{dc}{dC} = \frac{-c}{2}\left[\frac{1}{\rho}\frac{d\rho}{dC} + \frac{1}{\beta}\frac{d\beta}{dC}\right] \tag{2}$$

The quantity dρ/dC is always positive while dβ/dC is negative and positive. When $\left(\frac{1}{\rho}\right)\frac{d\rho}{dC}$ and $\frac{1}{\beta}\left(\frac{d\beta}{dC}\right)$ are both positive, the ultrasonic velocity decreases with concentration. If $\left(\frac{1}{\rho}\right)\frac{d\rho}{dC}$ is positive and (1/β)(dβ/dC) is negative and the net value is negative, the result is an increase in ultrasonic velocity with concentration. This can be illustrated in Fig. 1, in the case of abietate solution. The ultrasonic velocity increases with concentration meanings, the values of β decrease (as the ultrasonic velocity is the reciprocal of adiabatic compressibility) and the value of $\frac{d\beta}{dC}$ is negative. As a result eqn. 2 will be positive. So the decrease and increase in ultrasonic velocity shown in Fig. 1 depends upon the adiabatic compressibility which explains the packing of molecule in solution. The decrease in adiabatic compressibility means close packing of molecules in solution, which results an increase in ultrasonic velocity. That is why there are reverse cases of ultrasonic velocity before and after CMC. The different plots of ultrasonic velocity for different soaps are the indication of different type of packing of soap molecules in solution.

The variation in ultrasonic velocity, c with soap concentration, C, follows the relationship:

$$c = c_o + CG \tag{3}$$

where c_o = ultrasonic velocity in the pure solvent and G = Garnsey's constant[7]. The values of c_o and G were obtained from c *versus* C plots for the three soaps (Fig. 1) and are given in Table-1. The values of c_o and β_o (Table-2) obtained from c *versus* C and β *versus* C plots are in close agreement to the practial values for methanol, which confirms that the soaps do not aggregate appreciably below CMC, although the values change slightly with frequency.

The apparent molar compressibility φ_K of solutions is calculated using the relation[1]:

TABLE-1
VALUES OF c_o G, φ_K^o AND S_K OF LITHIUM SOAPS AT DIFFERENT FREQUENCIES IN METHANOL AT 35 ºC

Frequency (MHz)	c_o (m s^{-1})	G		$\varphi_K \times 10^{13}$	$S_K \times 10^{10}$	
		Below CMC	Above CMC		Below CMC	Above CMC
Abietate						
1	1072.0	541.7	-400.0	4422.5	-22.50	7.70
2	1070.0	500.0	-400.0	4440.0	-22.50	7.70
3	1069.0	500.0	-400.0	4450.0	-23.30	8.00
4	1068.0	500.0	-350.0	4460.5	-23.30	8.00
5	1066.6	500.0	-350.0	4480.5	-25.00	8.00
Oleate						
1	1072.5	-692.3	500.0	4090.0	31.29	-19.80
2	1070.5	-692.3	500.0	4085.0	31.29	-20.80
3	1069.8	-692.3	500.0	4055.0	35.00	-26.00
4	1068.5	-692.3	500.0	4080.0	35.00	-26.60
5	1067.3	-769.2	450.0	4115.0	38.33	-25.00
Myristate						
1	1073.0	500.0	-350.0	3330.0	-20.00	12.50
2	1070.0	500.0	-500.0	3350.0	-17.50	16.50
3	1069.0	500.0	-500.0	3380.0	-19.17	16.50
4	1068.0	500.0	-300.0	3390.0	-19.17	16.50
5	1065.0	500.0	-300.0	3462.5	-19.17	16.50

TABLE-2
EXTRAPOLATED AND EXPERIMENTAL VALUES OF ULTRASONIC VELOCITY AND ADIABATIC
COMPRESSIBILITY IN METHANOL FROM c *versus* C AND β *versus* C PLOTS RESPECTIVELY

Frequency (MHz)	Value in methanol alone	Experimental values of c_o			Value in methanol alone $\beta_o \times 10^{10}$	Experimental values of $\beta_o \times 10^{10}$		
		Abietate	Oleate	Myristate		Abietate	Oleate	Myristate
1	1072.0	1072.0	1072.5	1073.0	11.176	11.170	11.171	11.170
2	1070.0	1070.0	1070.5	1070.0	11.218	11.212	11.215	11.217
3	1069.0	1069.0	1069.8	1069.0	11.239	11.230	11.237	11.231
4	1068.0	1068.0	1068.5	1068.0	11.260	11.265	11.260	11.264
5	1067.0	1066.6	1067.3	1065.0	11.281	11.280	11.278	11.282

$$\varphi_K = \frac{1000(\rho_o\beta - \beta_o\rho)}{\rho\rho_o} + \frac{\beta M}{\rho} \tag{4}$$

In eqn. 4, M = molecular weight of the solute and ρ_o and β_o are the density and compressibility of the solvent, respectively. The apparent molar compressibility, φ_K, is related to the molar concentration, C, of soaps for the dilute solution by the relationship:

$$\varphi_K = \varphi_K^o + S_K C \tag{5}$$

where φ_K^o = limiting molar compressibility and S_K = constant. The values of φ_K^o and S_K as evaluated from $\varphi_K - C$ (Fig. 3) plots are given in Table-1. The value of φ_K^o increases with the increase in number of carbon atoms. The values of S_K in oleate are positive while the values for abietate and myristate are negative below the CMC, due to more soap-solvent interaction with oleate than with abietate and myristate. This is due to the close packing of molecules of oleate in solution, a conclusion, which is also supported by the high values of adiabatic compressibility for oleate.

The intermolecular free length, L_f, has been calculated using a semi-empirical formula given by Jacobson[8] based on the specific acoustic impedance, Z, Z = ρc. The values of L_f decrease up to the critical micelle concentration and then increase after this concentration for abietate and myristate while the reverse occurs for oleate. The decrease and increase in L_f values (Table-3) can be explained on the basis of electro-philic and electro-phobic interaction, respectively. For abietate and myristate, effects of concentration on L_f values decrease
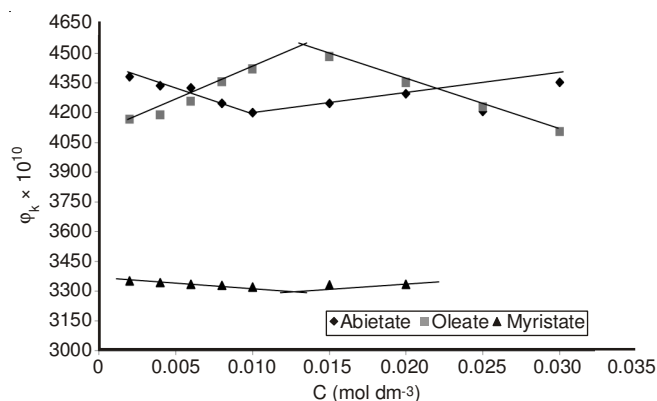

Fig. 3. Plots of φ_k *versus* C of lithium soaps in methanol at frequency 1 MHz at 35 ºC

with increase in concentration up to CMC while reverse case above the CMC, this are due to the electro-phobic interaction of soap molecules with solvent molecule but at higher concentration of soap electro-philic effect between soap molecules is larger. While in the case of oleate, L_f values increase with concentration up to the CMC, due to increasing effect of close packing of molecule with concentration. Also, the L_f values increase with increase of frequency.

The specific acoustic impedance varies in a similar way as does the ultrasonic velocity, c. The molar sound velocity, R (Rao constant)[1] and molar sound compressibility, W (Wada constant)[1] (Table-3), have been calculated from:

TABLE-3
ULTRASONIC VELOCITY AND ALLIED PARAMETERS FOR LITHIUM SOAPS IN METHANOL AT FREQUENCY 1 MHz AT 35 ºC

Conc. (mol dm^{-3})	c (m s^{-1})	$\beta \times 10^{10}$ (m^2 n^{-1})	$\phi_k \times 10^{13}$ (m^5 N^{-1} Kg mol^{-1})	L_f (Å)	$Z \times 10^{-3}$ (Kg m^{-2} s^{-1})	$R \times 10^3$ (m^3/mol(m/s)$^{1/3}$)	$W \times 10^3$ (m^3/mol(N/ m^2)$^{1/7}$)	n_s	$\alpha/f^2 \times 10^8$ (poise Kg^{-1} s^{-3})	$\alpha \times 10^{-4}$ (poise Kg^{-1} s^{-5})
Abietate										
0.002	1073	11.152	4382.5	49.39	835.7	421.0	781.6	11659.9	12.9905	12.9905
0.004	1074	11.128	4336.6	49.34	836.7	421.3	782.2	5827.3	12.9823	12.9823
0.006	1074	11.125	4326.3	49.33	836.9	421.4	782.5	3882.9	12.0107	13.0107
0.008	1076	11.081	4247.0	49.24	838.7	421.9	783.3	2911.1	12.9664	12.9664
0.010	1077	11.057	4200.9	49.18	839.8	422.2	783.9	2327.9	12.9585	12.9586
0.015	1075	11.091	4247.1	49.26	838.7	422.4	784.4	1549.3	13.0873	13.0873
0.020	1073	11.126	4295.0	49.34	837.6	422.7	785.0	1160.1	13.2174	13.2174
0.025	1072	11.140	4207.2	49.37	837.3	423.0	785.8	955.4	13.3112	13.3112
0.030	1070	11.155	4354.3	49.45	836.3	423.3	786.4	770.9	13.4434	13.4434
Oleate										
0.002	1071	11.194	4165.9	49.49	834.9	420.7	781.2	11658.5	13.0923	13.0923
0.004	1070	11.210	4188.6	49.52	833.5	420.7	781.4	5825.5	13.1572	13.1572
0.006	1068	11.253	4256.4	49.62	832.1	420.7	781.3	3880.6	13.2602	13.2602
0.008	1065	11.315	4356.0	49.75	829.9	420.5	781.1	2908.0	13.4012	13.4012
0.010	1063	11.356	4421.3	49.84	828.4	420.5	781.1	2324.4	13.5062	13.5062
0.015	1061	11.396	4482.6	49.93	827.1	420.8	781.2	1546.7	13.6416	13.6416
0.020	1064	11.324	4351.7	49.77	829.9	421.6	783.3	1158.9	13.5848	13.5848
0.025	1067	11.255	4228.1	49.62	832.7	422.5	784.9	926.0	13.5279	13.5279
0.030	1070	11.186	4104.8	49.47	835.5	423.4	786.5	771.1	13.4719	13.4719
Myristate										
0.002	1074	11.133	3350.0	49.35	836.3	421.1	781.7	11662.2	12.9542	12.9542
0.004	1075	11.110	3342.5	49.30	837.3	421.5	782.2	5828.8	12.9461	12.9461
0.006	1076	11.088	3335.2	49.25	838.2	421.7	782.7	3884.5	12.9384	12.9384
0.008	1077	11.066	3328.2	49.20	839.1	421.9	783.2	2912.1	12.9305	12.9305
0.010	1078	11.042	3320.1	49.15	840.1	422.2	783.7	2329.0	12.9223	12.9223
0.015	1076	11.081	3331.1	49.24	838.7	422.5	784.5	1550.2	13.0569	13.0569
0.020	1075	11.097	3334.5	49.27	838.3	422.5	784.7	1161.3	13.1439	13.1439

$$R = \left(\frac{M}{\rho}\right)c^{1/3} \qquad (6)$$

$$W = \left(\frac{M}{\rho}\right)\beta^{-1/7} \qquad (7)$$

where M = average molecular weight of solution calculated from the relation $M = X_1M_1 + X_2M_2$, X_1 and X_2 are the mole fractions of solute and solvent and M_1 and M_2 are their respective molecular weights.

The values of R and W increase with increasing concentration and decrease with increasing frequency.

The adiabatic compressibility data have been used to calculate the solvation number, n_s of soap by using Pasynskii's relation[9]:

$$n_s = \left(\frac{n_1}{n_2}\right)\left(\frac{1-V\beta}{n_1 V_1^o \beta^o}\right) \qquad (10)$$

where V = molar volume of the solution containing n_2 moles and V_1^o = value is the molar volume of solvent and n_1 = moles of solvents.

The values of solvation number, n_s (Table-3) are lower than in water, which show that the soaps dissociate less in methanol as compare to water.

The density of lithium soaps in methanol increases with increase in concentration (Fig. 2) and decreases with increase in temperature. The values of density for different soaps are in the order: abietate > oleate > myristate. Plots of ρ *versus* C show an intersection of two straight lines at CMC. The values of

CMC remain same as in case of ultrasonic velocity measurements and in water solvent. The extrapolated values of density for zero soap concentration, ρ_o is approximately equal to the corresponding experimental values of densities of methanol at 35-50 ºC. This indicates that the soap molecules do not aggregate below CMC.

Root's equation $((\rho-\rho_o)/C = A-BC^{1/2})$ has been used to study the behaviour of soap[9]. When $(\rho-\rho_o)/C$ is plotted against $C^{1/2}$ (Fig. 4), the plots obtained for abietate and myristate are linear below the CMC but curved above the CMC, while the plot of oleate shows an intersection of two straight lines at CMC.

The constants A and B (Table-2) have been calculated from the intercept and slopes of the straight lines below CMC. The values of 'A' decrease in abietate while increase in oleate and myristate. The constant 'B' does not change consistently with temperature.

The solute-solute interaction and solute-solvent interactions for abietate and oleate are similar to those in aqueous solution[1]. The solute-solvent interaction in myristate increases with temperature while solute-solute interaction is not appreciably observed due to non-linearity of the curve above CMC.

Apparent molar volume ϕ_v[1] has been determined by the equation:

$$\phi_v = \frac{M}{\rho_0} - \frac{(\rho - \rho_o)10^3}{\rho\rho_o} \qquad (7)$$

where M = molecular weight of soap. There are many factors, which contribute to changes in apparent molar volume such

TABLE-4

VALUES OF A, B, φ_v^o AND S_v FROM DENSITY DATA OF LITHIUM SOAPS IN METHANOL AT DIFFERENT TEMPERATURES

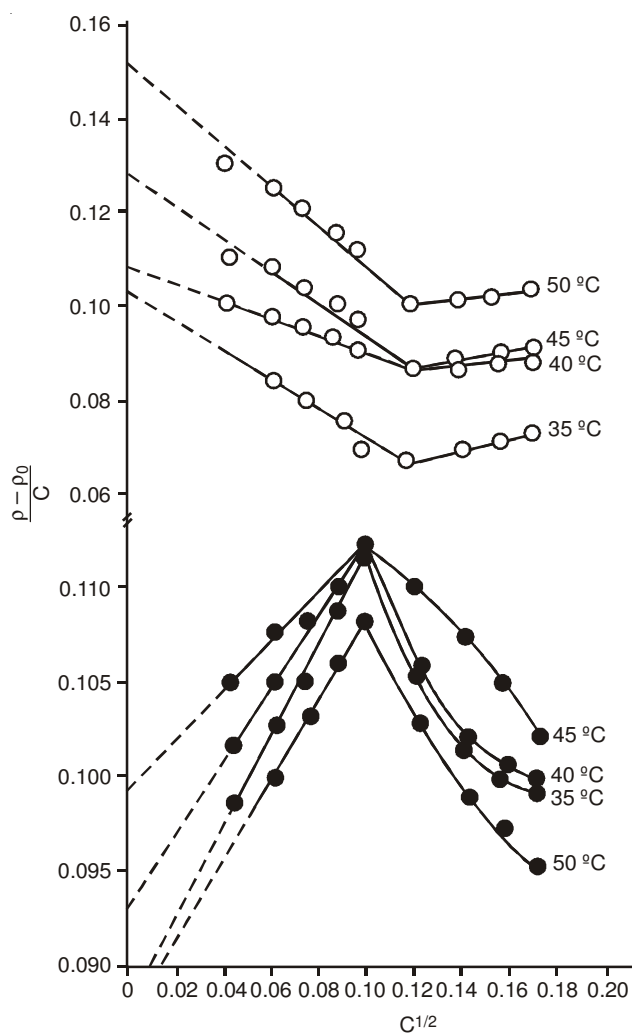| Soap	Temperature (ºC)	A	B	φ_v^o	S_v
Abietate	35	0.0992	0.1300	269.2	-170.0
	40	0.0930	0.1875	278.0	-242.5
	45	0.0877	0.2313	284.8	-295.0
	50	0.0872	0.2875	286.6	-255.0
Oleate	35	0.1040	- 0.3000	232.0	562.5
	40	0.1085	-0.1875	230.0	237.5
	45	0.1285	-0.3375	214.0	350.0
	50	0.1530	-0.4250	182.0	462.5
Myristate	35	0.0515	0.1875	233.0	-212.5
	40	0.0615	0.2000	224.0	-275.0
	45	0.0655	0.3050	218.0	-400.0
	50	0.0825	0.2750	196.8	-331.2

Fig. 4.   Plots of $(\rho-\rho_o)/C$ *versus* $C^{1/2}$ of lithium soaps in methanol at different temperatures. '●' Abietate '○' oleate

solutions are linear below CMC while they are non-linear above the CMC. The values of φ_v^0 and S_v (Table-4) obtained from the slope and intercepts of the plots having same behaviour as A and B (Table-4) constants of Root's equation, as B and φ_v indicate for solute-solvent interaction and A and S_v indicate solute-solute interaction.
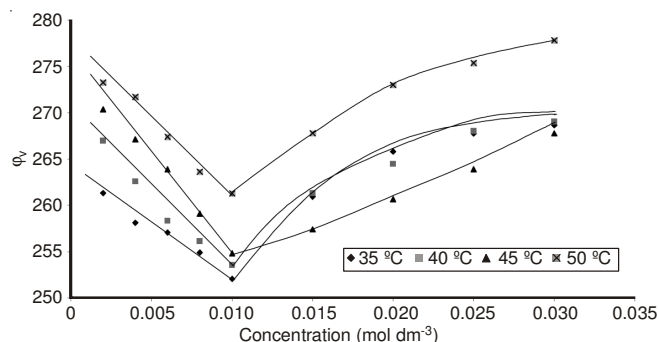

Fig. 5.   Plots of apparent molar volume, φ_v *verses* concentration, C of lithium abietate in methanol at different temperatures

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as solvation of amphiphilic solutes, nature of the ionic head group and the length of the non-polar portion of amphiphilic solutes. The plots of φ_v *versus* $C^{1/2}$ (Fig. 5) for dilute soap