Micellar Behavior of Neodymium Soaps in Methanol

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Synopsis

Neodymium butyrate, valerate, and caproate behave as simple electrolytes in dilute solutions and the CMC was found to decrease with increasing chain length of fatty acid constituent of the soap molecule. The CMC, degree of dissociation, and dissociation constant of neodymium soaps in methanol have been determined by conductometric measurements. The viscosity results have been explained on the basis of the equations proposed by Einstein, Vand, Moulik, and Jones and Dole. The values of the molar volume calculated by Einstein's and Vand's equations are in agreement with each other.

INTRODUCTION

The most striking feature of metal soaps is their increasing importance in various industries. The studies on higher rare earth metal carboxylates have not been carried out systematically so far with the result that only a few references[1-20] are available in this field.

The present work deals with the study of the conductivity and viscosity of the solutions of neodymium butyrate, valerate, and caproate in methanol. The work has been initiated with a view to study the micellar behavior and evaluate the various parameters.

EXPERIMENTAL

The chemicals used were of BDH/AR grade. Neodymium soaps were prepared by direct metathesis of corresponding potassium soap with slight excess of aqueous solution of neodymium nitrate at 50–55°C. The purity of the soaps was checked by the estimation of carbon, hydrogen, and metal contents and by the determination of melting points (butyrate 95°C, valerate 97°C, and caproate 101°C) of the soaps. The absence of hydroxyl groups in these soaps was confirmed by IR spectra. The reproducibility of the results was checked by preparing two samples of the same soaps under similar conditions.

A digital conductivity meter (Toshniwal CL 01.10 A) and a dipping type conductivity cell with platinized electrodes were used for measuring the conductance of the soap solutions. All the measurements were made at a constant temperature (40 ± 0.05°) in a thermostat.

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RESULTS AND DISCUSSION

Specific Conductance *k*

The specific conductance of the solutions of neodymium soaps (butyrate, valerate, and caproate) in methanol increases with increasing soap concentration and decreasing chainlength of fatty acid constituent of the soap. (Tables I–III.) The increase in the specific conductance with increase in soap concentration may be due to the ionization of neodymium soaps into simple metal cations, Nd^{3+} and fatty acid anions, R COO^- (where R is C_3H_7, C_4H_9, and C_5H_{11} for butyrate, valerate, and caproate, respectively) in dilute solutions and due to the formation of micelles at higher soap concentrations. The decrease in specific conductance with increasing chainlength of soap may be due to the increasing size and decreasing mobility of anions with increasing chainlength of the soap. The plots of specific conductance vs. soap concentration (Fig. 1) are characterised by a break which corresponds to the CMC of neodymium soaps (Table IV).

Molar Conductance μ and Dissociation Constant *K*

The molar conductance μ of the dilute solutions of neodymium soaps in methanol decreases with the increase in soap concentration (Tables I–III). The decrease in molar conductance may be due to the combined effects of ionic atmosphere, solvation of ions, decrease of mobility and ionization, and formation of micelles. The plots of molar conductance μ vs. square root of soap concentration, $C^{1/2}$, are not linear, which indicates that these soaps do

TABLE I
Conductometric Data of Neodymium Butyrate in Methanol at 40 ± 0.05°C

Sample no.	Concentration $C \times 10^3$ (g mol L^{-1})	Specific conductance $k \times 10^6$ (mhos)	Molar conductance μ	Degree of dissociation α	Dissociation constant $K \times 10^6$
1	7.1	77.0	10.84	0.638	4.4
2	8.0	82.0	10.25	0.603	4.6
3	8.9	86.0	9.66	0.568	4.6
4	10.0	92.0	9.20	0.541	5.0
5	11.9	102.0	8.57	0.504	5.9
6	13.1	108.0	8.24	0.485	6.5
7	14.7	114.0	7.76	0.456	6.8
8	16.6	123.0	7.41	0.436	7.9
9	17.8	128.0	7.19	0.423	8.4
10	19.2	133.0	6.93	0.408	8.9
11	20.8	139.0	6.68	0.393	9.5
12	22.7	145.0	6.39	0.376	10.1
13	25.0	153.0	6.12	0.360	11.1
14	27.7	162.0	5.85	0.328	9.9
15	31.3	172.0	5.50	0.324	13.5
16	35.7	184.0	5.15	0.303	14.9
17	41.7	199.0	4.77	0.281	17.0
18	50.0	224.0	4.48	0.264	22.3

TABLE II
Conductometric Data of Neodymium Valerate in Methanol at 40 ± 0.05°C

Sample no.	Concentration $C \times 10^3$ (g mol L^{-1})	Specific conductance $k \times 10^6$ (mhos)	Molar conductance μ	Degree of dissociation α	Dissociation constant $K \times 10^6$
1	7.1	64.3	9.06	0.599	3.1
2	8.0	68.3	8.54	0.564	3.2
3	8.9	71.9	8.08	0.534	3.3
4	10.0	75.9	7.59	0.502	3.4
5	11.9	83.1	6.98	0.461	3.8
6	13.1	87.4	6.67	0.441	4.1
7	14.7	92.7	6.31	0.417	4.4
8	16.6	98.7	5.95	0.393	4.9
9	17.8	102.3	5.75	0.380	5.1
10	19.2	106.3	5.54	0.366	5.4
11	20.8	110.8	5.33	0.352	5.8
12	22.7	115.8	5.10	0.337	6.1
13	25.0	121.5	4.86	0.321	6.6
14	27.7	128.2	4.63	0.306	7.2
15	31.3	136.0	4.35	0.288	8.0
16	35.7	145.5	4.10	0.271	9.1
17	41.7	156.8	3.74	0.247	9.7
18	50.0	180.0	3.60	0.238	14.2

TABLE III
Conductometric Data of Neodymium Caproate in Methanol at 40 ± 0.05°C

Sample no.	Concentration $C \times 10^3$ (g mol L^{-1})	Specific conductance $k \times 10^6$ (mhos)	Molar conductance μ	Degree of dissociation α	Dissociation constant $K \times 10^6$
1	7.1	42.0	5.92	0.459	0.79
2	8.0	44.0	5.50	0.426	0.79
3	8.9	45.4	5.10	0.395	0.77
4	10.0	49.7	4.97	0.385	0.96
5	11.9	53.4	4.49	0.348	1.02
6	13.1	55.7	4.25	0.329	1.06
7	14.7	58.4	3.97	0.308	1.12
8	16.6	61.5	3.70	0.287	1.18
9	17.8	63.2	3.55	0.275	1.20
10	19.2	65.3	3.40	0.264	1.26
11	20.8	67.4	3.24	0.251	1.29
12	22.7	69.9	3.08	0.239	1.35
13	25.0	71.9	2.88	0.223	1.34
14	27.7	77.1	2.78	0.216	1.59
15	31.3	81.4	2.60	0.202	1.73
16	35.7	86.3	2.42	0.188	1.89
17	41.7	92.9	2.23	0.173	2.12
18	50.0	98.9	1.98	0.153	2.18

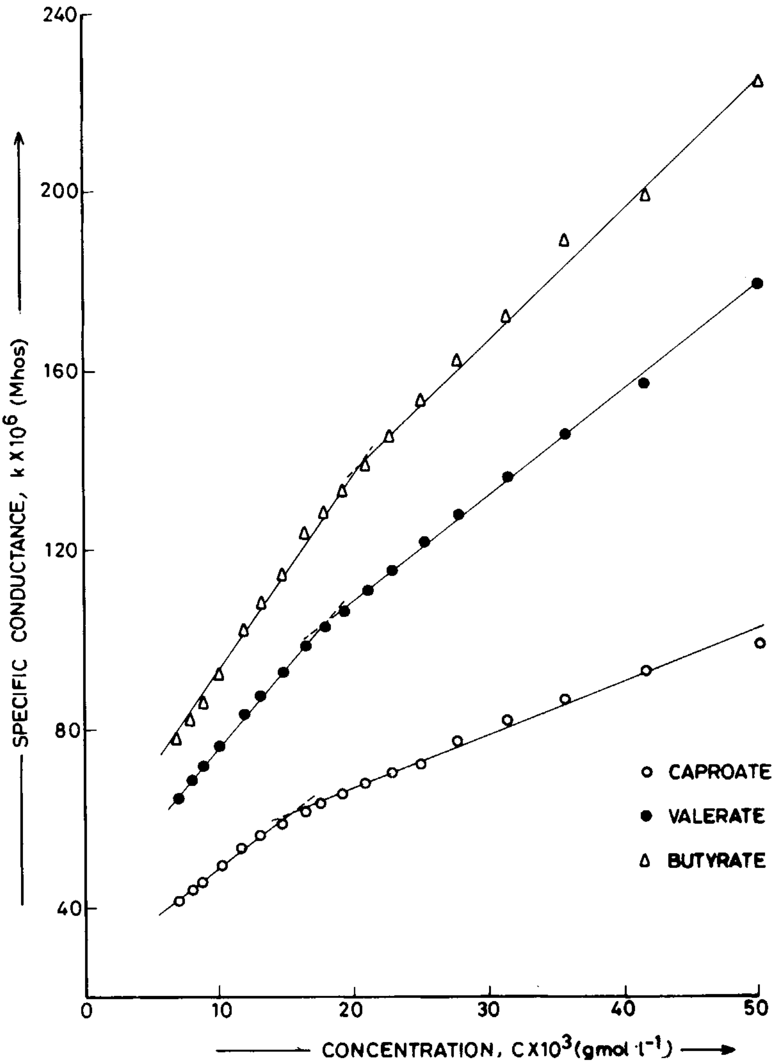

Fig. 1. Specific conductance vs. concentration of neodymium soaps in methanol.

TABLE IV
Values of CMC, Limiting Molar Conductance and Dissociation Constant of Neodymium Soaps

Name of soap	In methanol		
	CMC (mol L^{-1})	μ_0	$K \times 10^6$
Caproate	0.015	12.9	2.30
Valerate	0.018	15.1	1.09
Butyrate	0.021	17.0	0.60

not behave as strong electrolyte in solutions. The molar conductance of the solutions of neodymium soaps increases with decreasing chainlength of the fatty acid constituent of soap but the nature of the curves for these soap solutions remains the same.

The soap in dilute solutions behaves as a simple electrolyte and so an expression for the dissociation of neodymium soaps can be developed in Ostwald's manner. If C is the concentration (mol L^{-1}) and α is the degree of dissociation of neodymium soap, the equivalent concentrations of different species can be represented as

$$\begin{array}{ccc} Nd(RCOO)_3 & \rightleftharpoons Nd^{+3} & + \; 3RCOO^- \\ C(1-\alpha) & C\alpha & 3(C\alpha) \end{array} \quad (1)$$

where R is C_3H_7, C_4H_9, and C_5H_{11} for butyrate, valerate, and caproate, respectively. The dissociation constant K can be expressed as

$$K = \frac{[Nd^{+3}][RCOO^-]^3}{[Nd(RCOO)_3]}$$

$$= \frac{C\alpha(3C\alpha)^3}{C(1-\alpha)} = \frac{27C^3\alpha^4}{(1-\alpha)}$$

Since the ionic concentrations are low and the interionic effects are almost negligible in dilute solutions, the solutions will not deviate appreciably from ideal behavior and so the activity of ions can be taken as almost equal to the concentration. The degree of dissociation may be replaced by the conductance ratio, μ/μ_0, where μ is the molar conductance at finite concentration and μ_0 is the limiting molar conductance at infinite dilution. On substituting the value of α and rearranging, eq. (1) can be written as

$$\mu^3C^3 = \frac{K\mu_0^4}{27\mu} - \frac{K\mu_0^3}{27} \quad (2)$$

The plots of μ^3C^3 vs. $1/\mu$ show that the values of μ^3C^3 increase slowly and linearly in dilute solutions but increase rapidly in concentrated solutions. The values of dissociation constant K and limiting molar conductance μ_0 have been obtained from the slope $K\mu_0^4/27$ and intercept $-K\mu_0^3/27$ of the linear portion of the plots of μ^3C^3 vs. $1/\mu$ for dilute soap solution and are recorded in Table IV. The values of limiting molar conductance μ_0 decrease and dissociation constant K increase with the increase in the chain length of the soap. The values of degree of dissociation, α, at different soap concentrations have been calculated by assuming it as equal to the conductance ratio μ/μ_0. The plots of the degree of dissociation vs. soap concentration show that the degree of dissociation of these soaps decreases rapidly in dilute solutions with the increasing soap concentration. The dissociation constant K calculated by using eq. (1) and assuming the degree of dissociation as equal to the conductance ratio are recorded in Tables I–III. The values show that dissociation

TABLE V
Density and Viscosity of Neodymium Butyrate in Methanol at 40 ± 0.05°C

Sample no.	Concentration $C \times 10^3$ (g mol L^{-1})	Density ρ (g mL^{-1})	Viscosity η (cP)	Specific viscosity $\eta_{sp} \times 10^3$	η_{sp}/C	$\eta_{sp}/C^{1/2}$	$(\eta/\eta_0)^2$	$1/\log(\eta/\eta_0)$
1	2	0.7974	0.539	7.5	3.75	0.17	1.02	309.1
2	4	0.8014	0.543	15.0	3.75	0.24	1.03	155.1
3	6	0.8052	0.548	24.3	4.05	0.32	1.05	95.9
4	8	0.8086	0.552	31.8	3.98	0.36	1.06	73.6
5	10	0.8128	0.558	43.0	4.30	0.43	1.09	54.7
6	20	0.8312	0.579	82.2	4.11	0.58	1.17	29.1
7	30	0.8474	0.600	121.5	4.05	0.70	1.26	20.1
8	40	0.8638	0.618	155.1	3.88	0.78	1.33	16.0
9	50	0.8782	0.640	196.3	3.93	0.88	1.43	12.9

constant K decreases with increasing chainlength of the soap (Tables I–III). The values of dissociation constant K show approximate constancy in dilute solutions but exhibit a drift with increasing soap concentrations which shows that the soap does not behave as a very weak electrolytes. The drift in the values of dissociation constant with increasing soap concentration may be partly due to the fact that the degree of dissociation α is not exactly equal to the conductance ratio μ/μ_0 and mainly due to the fact that the activity coefficients of ions are not exactly equal to unity.

Density

The density of the solutions of neodymium soaps (caproate, valerate, and butyrate) in methanol increases with increasing soap concentration and with the number of carbon atoms in the soap molecule (Tables V–VII). The plots of density vs. soap concentration (Fig. 2) are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC of the soap (Table VIII). The extrapolated values of the density ρ_0 (caproate: 0.7942, valerate: 0.7940, and butyrate: 0.7937 g mL^{-1}) are in

TABLE VI
Density and Viscosity of Neodymium Valerate in Methanol at 40 ± 0.05°C

Sample no.	Concentration $C \times 10^3$ (g mol L^{-1})	Density ρ (g mL^{-1})	Viscosity η (cP)	Specific viscosity $\eta_{sp} \times 10^3$	η_{sp}/C	$\eta_{sp}/C^{1/2}$	$(\eta/\eta_0)^2$	$1/\log(\eta/\eta_0)$
1	2	0.7992	0.541	11.2	5.5	0.24	1.02	206.5
2	4	0.8042	0.547	22.4	5.6	0.36	1.05	103.8
3	6	0.8106	0.553	33.6	5.6	0.44	1.07	69.6
4	8	0.8152	0.558	43.0	5.4	0.48	1.09	54.7
5	10	0.8208	0.564	54.2	5.4	0.54	1.11	43.6
6	20	0.8452	0.590	102.8	5.1	0.72	1.22	23.5
7	30	0.8612	0.610	140.2	4.7	0.81	1.30	17.6
8	40	0.8772	0.630	177.6	4.4	0.89	1.39	14.1
9	50	0.8932	0.650	215.0	4.3	0.96	1.48	11.8

TABLE VII
Density and Viscosity of Neodymium Caproate in Methanol at 40 ± 0.05°C

Sample no.	Concentration $C \times 10^3$ (g mol L^{-1})	Density ρ (g mL^{-1})	Viscosity η (cP)	Specific viscosity $\eta_{sp} \times 10^3$	η_{sp}/C	$\eta_{sp}/C^{1/2}$	$(\eta/\eta_0)^2$	$1/\log(\eta/\eta_0)$
1	2	0.8018	0.543	15.0	7.5	0.33	1.03	155.1
2	4	0.8092	0.550	28.0	7.0	0.44	1.06	83.3
3	6	0.8174	0.557	41.1	6.9	0.53	1.08	57.1
4	8	0.8246	0.564	54.2	6.8	0.61	1.11	43.6
5	10	0.8326	0.571	67.3	6.7	0.67	1.14	35.4
6	20	0.8608	0.597	115.9	5.8	0.82	1.25	21.0
7	30	0.8762	0.619	157.0	5.2	0.91	1.35	15.8
8	40	0.8940	0.639	194.4	4.9	0.97	1.43	13.0
9	50	0.9104	0.659	231.8	4.6	1.03	1.52	11.1

agreement with the experimental value of the density (0.7942 g mL^{-1} at 40°C) of the solvent.

Viscosity

The viscosity η and specific viscosity η_{sp} of the solutions of neodymium soaps in methanol increase with increasing soap concentration (Tables V–VII). The increase in viscosity (Fig. 3) may be due to the increasing tendency of the

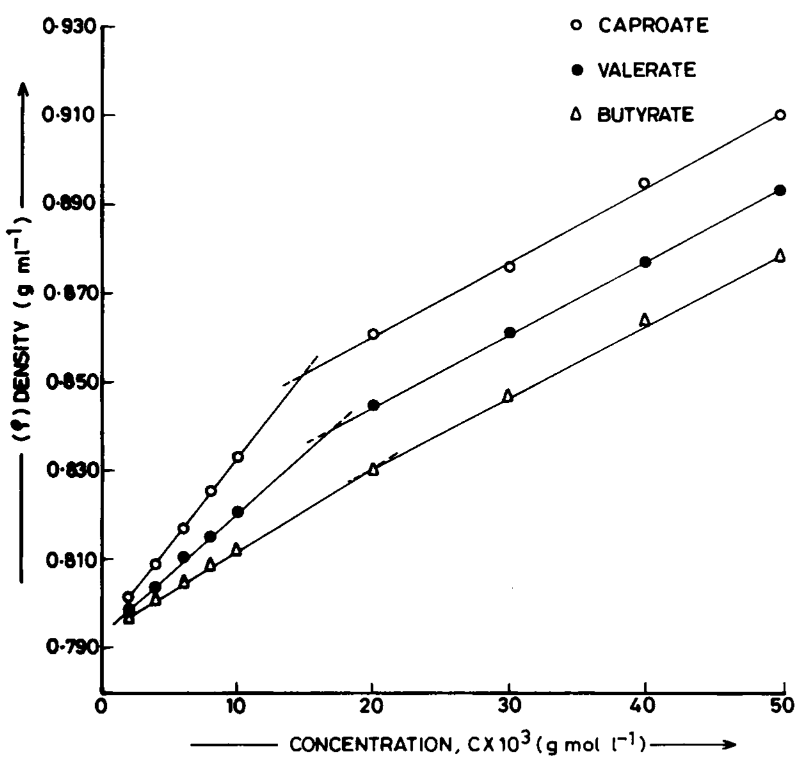

Fig. 2. Density vs. concentration of neodymium soaps in methanol.

TABLE VIII
Values of Various Parameters from Viscosity Measurements of Neodymium Soaps in Methanol at 40 ± 0.05°C

Sample no.	Name of soap	CMC (mol L^{-1})	$\bar{V}$ (Einstein's equation)	$\bar{V}$ (Vand's equation)	ϕ	M	K	A	B	η_I
1	Caproate	0.014	2.70	1.61	5	1.05	930	0.23	6.23	7.20
2	Valerate	0.017	2.20	2.44	5	1.04	830	0.16	5.77	5.74
3	Butyrate	0.021	1.65	3.02	5	1.02	707	0.10	4.29	4.36

soap molecules to form aggregates with the increase in soap concentration. The plots of viscosity η vs. soap concentration C and of specific viscosity η_{sp} vs. soap concentration C are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC of these soaps. The plots of viscosity η vs. soap concentration have been extrapolated to zero soap concentration and the extrapolated values of the viscosity η_0 (0.536 cP) are in agreement with the viscosity of methanol (0.535 cP at 40°C).

The viscosity results have been interpreted in terms of equations proposed by Einstein,[21] Vand,[22] Moulik,[23] and Jones and Dole[24]:

Einstein[21]: $$\eta_{sp} = 2.5\bar{V}C$$

Vand[22]: $$1/C = \left(\frac{0.921}{\bar{V}}\right)^{-1} \cdot \frac{1}{\log(\eta/\eta_0)} + \phi\bar{V}$$

Moulik[23]: $$(\eta/\eta_0)^2 = M + KC^2$$

Jones–Dole[24]: $$\frac{\eta_{sp}}{C^{1/2}} = A + BC^{1/2}$$

where $\bar{V}$, C, ϕ, η, η_0, and η_{sp} are the molar volume of the soap, concentration, interaction coefficient, viscosity of the solution, viscosity of the solvent, and specific viscosity, respectively.

The plots of specific viscosity η_{sp} vs. soap concentration C below the CMC are linear with intercept equal to zero, which shows that Einstein's equation is applicable to these soap solutions below the CMC. The molar volume of neodymium soaps calculated from the slope of plots are recorded in Table VIII. The values of the CMC obtained from the plots of η_{sp} vs. C are in agreement with the values obtained from density and viscosity data. The plots of η_{sp}/C vs. C below the CMC have been extrapolated to zero soap concentration and the extrapolated values (i.e., the intrinsic viscosity, η_I) increase with increasing chainlength of the soap molecules (Table VIII).

The values of molar volume calculated from the slope of the plots of $1/C$ vs. $1/\log(\eta/\eta_0)$ (Table VIII) are in agreement with the values calculated from Einstein's plots. The values of interaction coefficient ϕ have been calculated from the intercept of these plots and are found to be 5.0 for the solutions of neodymium soaps in methanol.

The plots of $(\eta/\eta_0)^2$ against C^2 show that Moulik's equation is applicable to the solutions of neodymium soaps. The values of Moulik's constant M and K have been obtained from the intercept and slope of these plots (Table

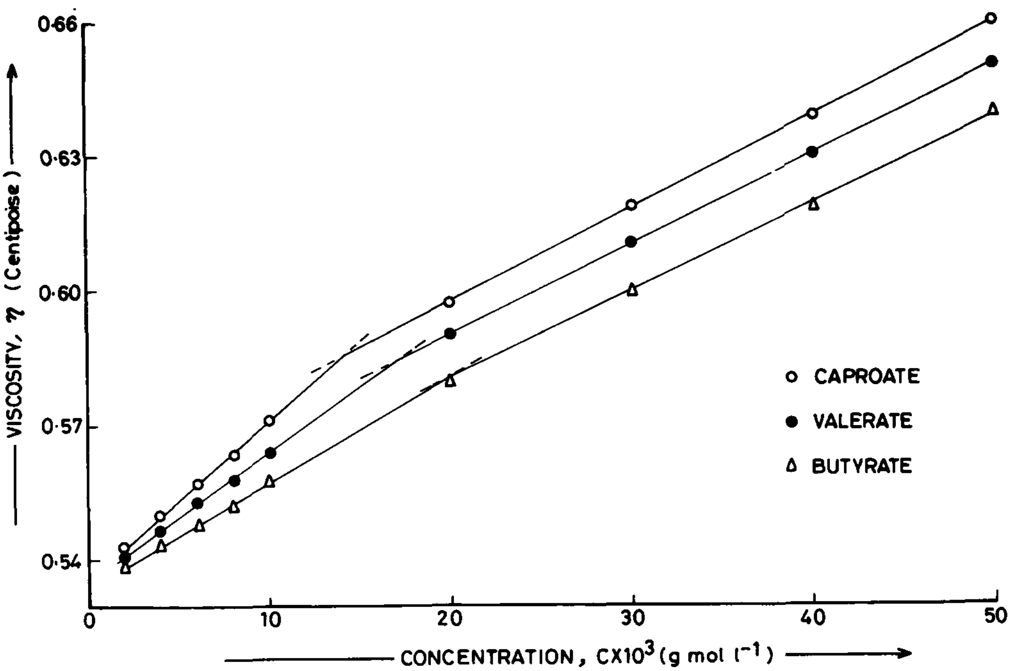

Fig. 3. Viscosity vs. concentration of neodymium soaps in methanol.

VIII). The values of M and K increase with increasing chainlength of soap molecules.

The plots of $\eta_{sp}/C^{1/2}$ vs. $C^{1/2}$ indicate a break at a definite soap concentration which corresponds to the CMC of the soap. The values of constants A and B obtained from the intercept and slope of these plots below the CMC are recorded in Table VIII. The values of the constant B (soap–solvent interaction) are larger than those of constant A (soap–soap interaction), which confirms that the soap molecules do not show appreciable aggregation of the soap molecules below this concentration.

It is, therefore, concluded that the viscosity results for the solutions of neodymium soaps may be satisfactorily explained in terms of equations proposed by Einstein, Vand, Moulik, and Jones and Dole.

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