

CHAPTER - III

Viscosity and Density of Solutions of Tetraalkylammonium Bromides, R_4NBr , (R = Butyl to Heptyl) in Tetrahydrofuran (THF) at different Temperatures.

Viscosities and densities are reported for tetraalkylammonium bromides in tetrahydrofuran (THF) at 25° and 35°C. The data have been used to calculate viscosity B-coefficients employing Jones-Dole, Breslau-Miller and Vand equations. Results show that tetraalkylammonium bromides can be approximated as spherical entities in tetrahydrofuran (THF) and act as structure-promoters.

Dependence of viscosity (η) on concentration (C) of solutes and temperature (T) of solutions has been employed as a function of studying ion-ion and ion-solvent interactions in non-aqueous solvents. It has been found by a number of workers¹⁻³ that the addition of electrolyte could either break or make the structure of a liquid. Since viscosity is a property of the liquid which depends upon the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures.

Experimental :

Tetrahydrofuran (Merck) was kept several days over KOH, then refluxed for 24 hours and distilled over $LiAlH_4$. Its boiling point, density and viscosity compared well with the literature values⁴. The specific conductance of THF was ca. 0.81×10^{-6}

$\Omega^{-1}\text{cm}^{-1}$ at 25°C.

Tetraalkylammonium salts (Fluka purum or puriss) were purified as described in the literature⁵ and also described earlier by us⁶ . The salts were purified by recrystallization and the higher homologues were recrystallized twice to ensure the highest purity. The recrystallized salts were dried under vacuum at elevated temperatures for 12 hours. All these salts were stored in a vacuum desiccator and dried for 4 hours at 100°C prior to use.

A stock solution for each salt (~ 0.1 M) in the solvent (THF) was prepared and the working solutions were obtained by weight dilution. The molar concentration of the solutions was calculated from molality and density values.

The densities were measured with an Ostwald- Sprengal type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 1 m.m. The pycnometer was calibrated at 25 and 35°C with doubly distilled water. The precision of the density measurements was $\pm 3 \times 10^{-5}$ g cm⁻³ . The measurements were made in an oil bath maintained with an accuracy of $\pm 0.005^\circ\text{C}$ of the desired temperature by means of a mercury-in-glass thermoregulator and the absolute temperature was determined by a platinum resistance thermometer and Muller bridge⁷ .

The kinematic viscosities were measured by means of suspended-level Ubbelohde⁸ viscometer with a flow time of about 539 sec for distilled water at 25°C. The time of the efflux was

measured with a stop watch capable of recording ± 0.1 sec. The viscometer was always kept in a vertical position in a water thermostat. The viscometer needed no correction for kinetic energy. The Kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equation :

$$\left. \begin{aligned} \nu &= ct - K/t \\ \eta &= \nu\rho \end{aligned} \right\} \quad (1)$$

Where t is the efflux time, ρ is the density and c and k are the characteristic constants of the viscometer. The values of the constants c and k , determined by using water and benzene as the calibrating liquids at 25 and 35°C were found to be $1.648 \times 10^{-5} \text{ cm}^2 \text{ s}^{-2}$ and -0.02331647 cm^2 respectively. The precision of the viscosity measurements was $\pm 0.05\%$. In all cases, the experiments were performed at least in five replicates and the results were averaged.

Relative viscosities (η_r) were obtained by using equation (2)

$$\eta_r = \eta/\eta_0 = \rho t / \rho_0 t_0 \quad (2)$$

Where $\eta, \eta_0, \rho, \rho_0$ and t, t_0 are the absolute viscosities, densities and flow times for the solution and solvent respectively.

The measurements were carried out in a thermostatic

bath maintained with an accuracy of $\pm 0.01^\circ\text{C}$ of the desired temperature.⁹ A 60W heating element and a toluene-mercury thermoregulator were used to maintain the temperature of the experimental thermostat which was placed in a hot-cum-cold thermostat. The temperature of the hot-cum-cold thermostat was preset at the desired temperature using a contact thermometer and relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.

Results and Discussion

Density (ρ), viscosity (η), and relative viscosity (η_r) data of tetraalkylammonium bromides (But₄ to Hept₄) in tetrahydrofuran (THF) at 25 and 35°C have been recorded in Table-1. It can be seen from the data that the values of viscosities of solutions increase with increasing concentration of the salt and decrease with increasing temperature.

The variation of relative viscosity (η_r) with concentration (c) is usually expressed by the Jones-Dole equation¹⁰

$$\eta_r = 1 + Ac^{\frac{1}{2}} + Bc \quad (3)$$

Since, in general, $A/B \ll 1$, the second term may be neglected at concentrations above 0.002 M and the equation (3) may be written as¹¹

$$\eta_r = 1 + Bc, \quad 0.002 < M < \sim 0.1 \quad (4)$$

In the present study, equation (4) is valid in solutions of concentration ranging between 0.01 and .08 M . The linearity obtained by plotting of η_r vs c is shown in Figs. 1 & 2. This type of characteristic is an indication of the applicability of equation (4). The values of B obtained from the slopes of the plots are given in Table - 2.

The relative viscosity data of solutions have been fitted into the following equations :

i) Moulik equation¹² ,

$$\eta_r^2 = M + k'c^2 \quad (5)$$

Where M and k' are constants. The applicability of Moulik equation is shown by the linear plots of η_r^2 vs c^2 (Figs. 3 & 4).

ii) Breslau-Miller equation¹¹ ,

$$\bar{V}_e = \frac{-2.5c + [(2.5c)^2 - 4 (10.05c^2)(1 - \eta_r)]^{\frac{1}{2}}}{2(10.05) c^2} \quad (6)$$

Where \bar{V}_e is the average effective rigid molar volume. The values of \bar{V}_e thus obtained were used for calculating B-coefficients, employing the following relation :

$$B = 2.90 \bar{V}_e - 0.018 \quad (7)$$

iii) Vand's equation ¹³,

$$\ln \eta_r = \frac{2.5 \phi}{1 - K\phi} \quad (8)$$

Where ϕ is volume fraction and K the generalised particle interaction coefficient. Substituting $\phi = C\bar{V}$ and rearranging equation (8), we have,

$$\frac{C}{\log \eta_r} = \frac{2.303}{2.5 \bar{V}} - \frac{2.303}{2.5} KC \quad (9)$$

Where \bar{V} is the effective flowing volume. \bar{V} has been obtained from the intercept of the linear plot of $C/\log \eta_r$ vs C, shown in Fig 5. B-coefficients were calculated from the relation,

$$B = 2.5 \bar{V} \quad (10)$$

B values thus calculated from equations (4), (7) and (10) are listed in Table - 2 for comparison. B values obtained from Jones-Dole and Breslau-Miller equations are more or less near to each other, however they differ considerably from those obtained from Vand-equation (9). This discrepancy as regards to the magnitude of B may be attributed to concentration dependence validity of viscosity equations and variable ion-solvent interaction with varying concentration of electrolyte. The familiar viscosity B-coefficients and the related ionic molar contribution to the free energy, enthalpy and entropy of activation are re-examined on the compensation principle by Feakins et al¹⁴. Particular attention is paid to the

nature of the solvent in the transition state. If compensation between enthalpic and entropic contributions from solute-induced structural changes occurs in both ground and transition state solvents, then free energy of activation, and hence B can not be influenced by changes in the structure of the solvent of the type proposed, say, by Frank and Wen¹⁵.

From Table - 2 it is seen that the B-values always increase from Bu_4NBr to Hept_4NBr in THF. This fact indicates that the larger tetraalkylammonium cations are scarcely solvated in this solvent medium.

Table - 2 also shows that B-values are positive and decrease with rise in temperature (negative dB/dT) suggesting¹⁶ structure-promoting tendency of tetraalkylammonium bromides. The positive B-values and negative dB/dT show the absence of a firm layer of solvent molecules around the ion-in their Co-sphere.

The investigation thus indicates that all the salts studied here exhibit strong ionic interactions, apparently due to the low dielectric constant of the solvent.

R E F E R E N C E S

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TABLE - 1

Concentration (M), Molality (m), Density (ρ), Flow-time (t), Viscosity (η) and relative viscosity (η_r) of Tetraalkylammonium Bromides in Tetrahydrofuran (THF) at different Temperatures

Salt - Bu_4NBr , Solvent - THF, Mol. Wt. = 322.38

Density of THF at 25°C = 0.88072 g /c.c. and viscosity at 25°C = 0.463 cP

Temperature = 25°C

Relative Viscosity (η_r)	Concentration (M)	Molality (m)	Density (ρ) g /cc	Viscosity (η) in cp	Flow-time in Sec.
1.11771	0.0740808	0.0857363	0.887936	0.5174982	349.60
1.08952	0.0550314	0.0633746	0.8860916	0.5044466	341.30
1.07592	0.0402152	0.0461349	0.8846517	0.4981549	337.50
1.0477916	0.0253991	0.0290268	0.8832077	0.4851275	329.00
1.0305875	0.0105829	0.0120486	0.881758	0.47716119	324.00

Density of THF at 35°C = 0.87033 gm/cc and viscosity at 35°C = 0.4277 cP

Temperature = 35°C

1.0972803	0.0731675	"	0.8769894	0.4693068	320.30
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Contd.....²

1.06722	0.0543603	"	0.8752872	0.4564507	311.90
1.05336	0.039729	"	0.8739585	0.4505072	308.20
1.0305268	0.0250946	"	0.8726254	0.4407563	301.80
1.0160601	0.0104571	"	0.871288	0.4345689	297.90

Salt - Pent₄NBr , Solvent - THF, Mol. Wt. = 378.49

Density of THF at 25°C = 0.88072 g /cc and viscosity at 25°C = 0.463 cP

Temperature - 25°C

1.13868	0.0750024	0.0873286	0.8872396	0.5272113	356.60
1.1045784	0.0568984	0.0658440	0.8856746	0.5114198	346.30
1.0851734	0.0413806	0.0476369	0.8843288	0.5024353	340.60
1.0624117	0.0258629	0.0296188	0.8829790	0.4918966	333.80
1.044985	0.0103451	0.117864	0.8816249	0.4838279	328.10

Density of THF at 35°C = 0.87033 g /cc and viscosity at 35°C = 0.4277 cP

Temperature - 35°C

1.27	0.0741108	"	0.8767008	0.481404	328.90
1.0886923	0.0562238	"	0.8751753	0.4656337	318.40

Contd.....3

1.0611672	0.0408906	"	0.8738592	0.4538612	310.60
1.0367141	0.025557	"	0.8725391	0.4434026	303.70
1.0255565	0.0102228	"	0.871215	0.4386305	300.80

Salt - Hex₄NBr, Solvent - THF, Mol. Wt. 434.60

Density of THF at 25°C = 0.88072 g /cc and viscosity at 25°C = 0.463 cP

Temperature - 25°C

1.173654	0.0748219	0.0875893	0.8867523	0.5434018	367.00
1.1229948	0.0555819	0.064551	0.8852089	0.5199466	352.00
1.0890423	0.0406176	0.0468834	0.8840048	0.50422661	342.00
1.0640546	0.0256532	0.0294306	0.8827974	0.4926573	334.40
1.0461546	0.0106888	0.0121887	0.8815868	0.4843696	329.00

Density of THF at 35°C = 0.87033 g /cc and viscosity at 35°C = 0.4277 cP

Temperature - 35°C

1.1653028	0.0739544	"	0.8764726	0.4983999	340.90
1.096575	0.0549794	"	0.8750279	0.4690051	320.60
1.068228	0.0401673	"	0.8737069	0.4568812	312.60

Contd.....4

1.04164	0.0253621	"	0.8724819	0.4455089	305.10
1.0281316	0.0105646	"	0.8711539	0.4397319	301.00

Salt - Hept₄NBr, Solvent - THF, Mol. Wt. = 490.71

Density of THF at 25°C = 0.88072 g /cc and viscosity at 25°C = 0.463 cP

Temperature - 25°C

1.1947177	0.0743343	0.0875131	0.8858836	0.5531543	367.90
1.1262201	0.0552197	0.0643988	0.8845615	0.5314399	353.70
1.0941359	0.0403529	0.0467194	0.8835305	0.5065849	343.80
1.064933	0.0254860	0.0292945	0.8824971	0.493064	334.80
1.0475546	0.0106191	0.0121187	0.8814613	0.4850178	330.50

Density of THF at 35°C = 0.87033 g /cc and viscosity at 35°C = 0.4277 cP

Temperature - 35°C

1.1853914	0.0735101	"	0.8760623	0.5069919	347.30
1.1125675	0.0545975	"	0.8745946	0.4758451	325.80
1.079246	0.0398925	"	0.8734501	0.4615935	316.20
1.0513299	0.0251915	"	0.8723028	0.4496538	308.20
1.0287877	0.0104948	"	0.8711529	0.4400125	301.80

TABLE - 2

Values of B^* from various equations at different temperatures

Salts	Temperatures					
	25°C			35°C		
	B^a	B^b	B^c	B^a	B^b	B^c
Bu ₄ NBr	1.346	1.798	2.280	1.228	1.345	1.616
Pent ₄ NBr	1.498	2.070	2.558	1.372	1.603	2.056
Hex ₄ NBr	1.715	2.305	2.677	1.553	1.773	2.326
Hept ₄ NBr	1.951	2.535	2.878	1.832	1.933	2.587

* Obtained from : ^a Jones-Dole equation; ^b Breslau-Miller's eqn. ; ^c Vand equation;

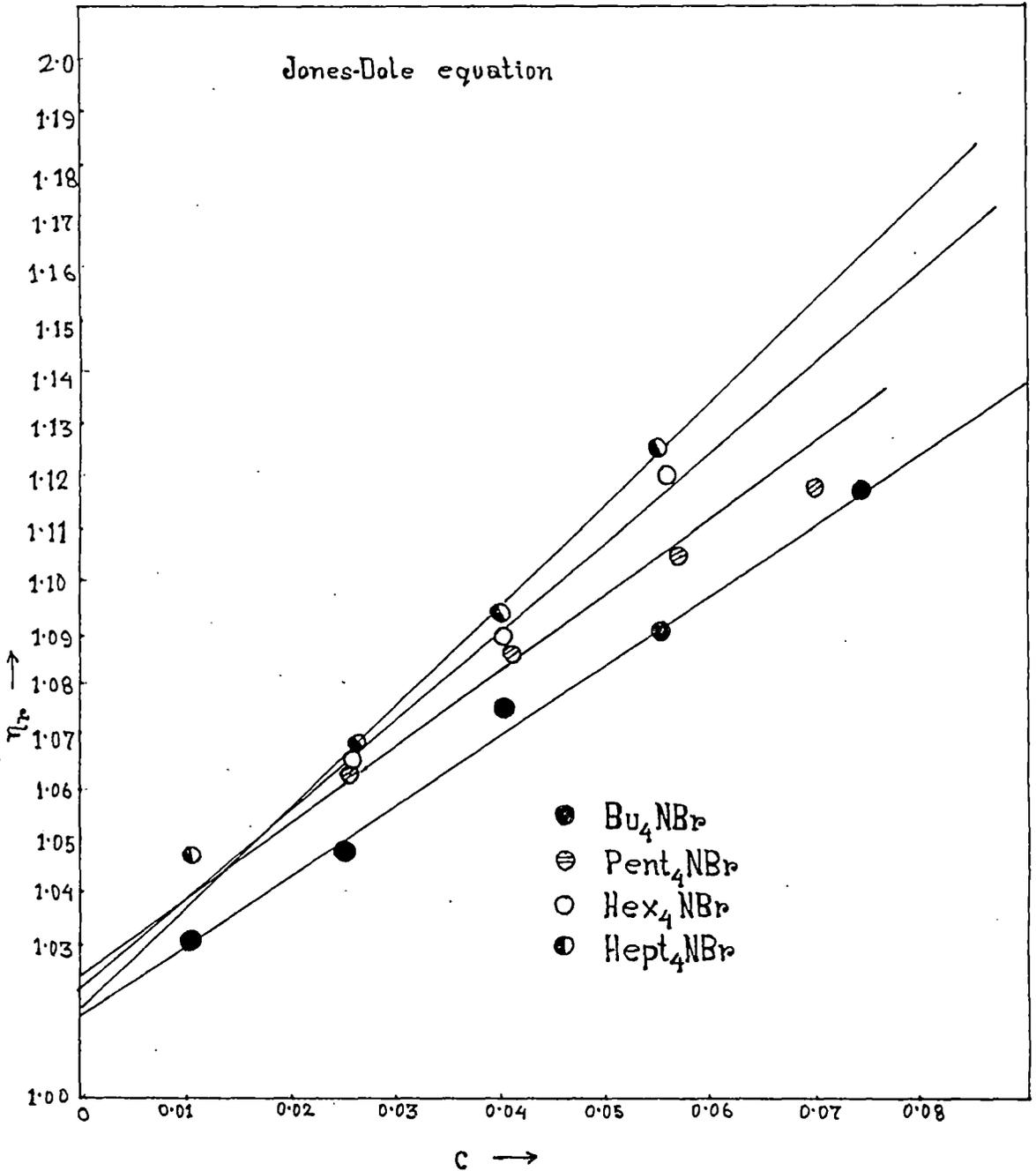
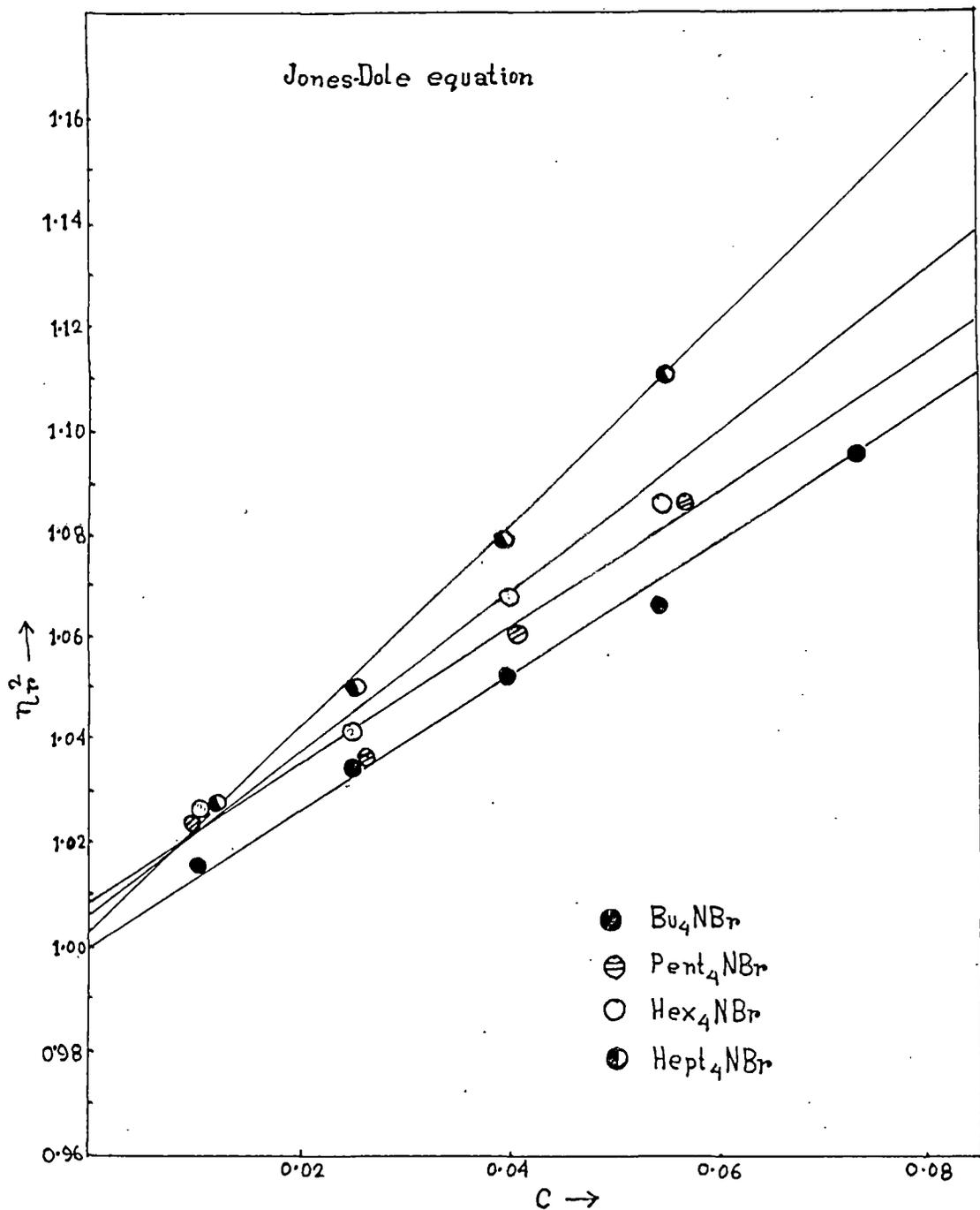


Fig-1 Plots of η_{sp} vs C for different tetraalkylammonium bromides in THF at 25°C.



Fig—2 Plots of η_r vs C for different tetraalkylammonium bromides in THF at 35°C .

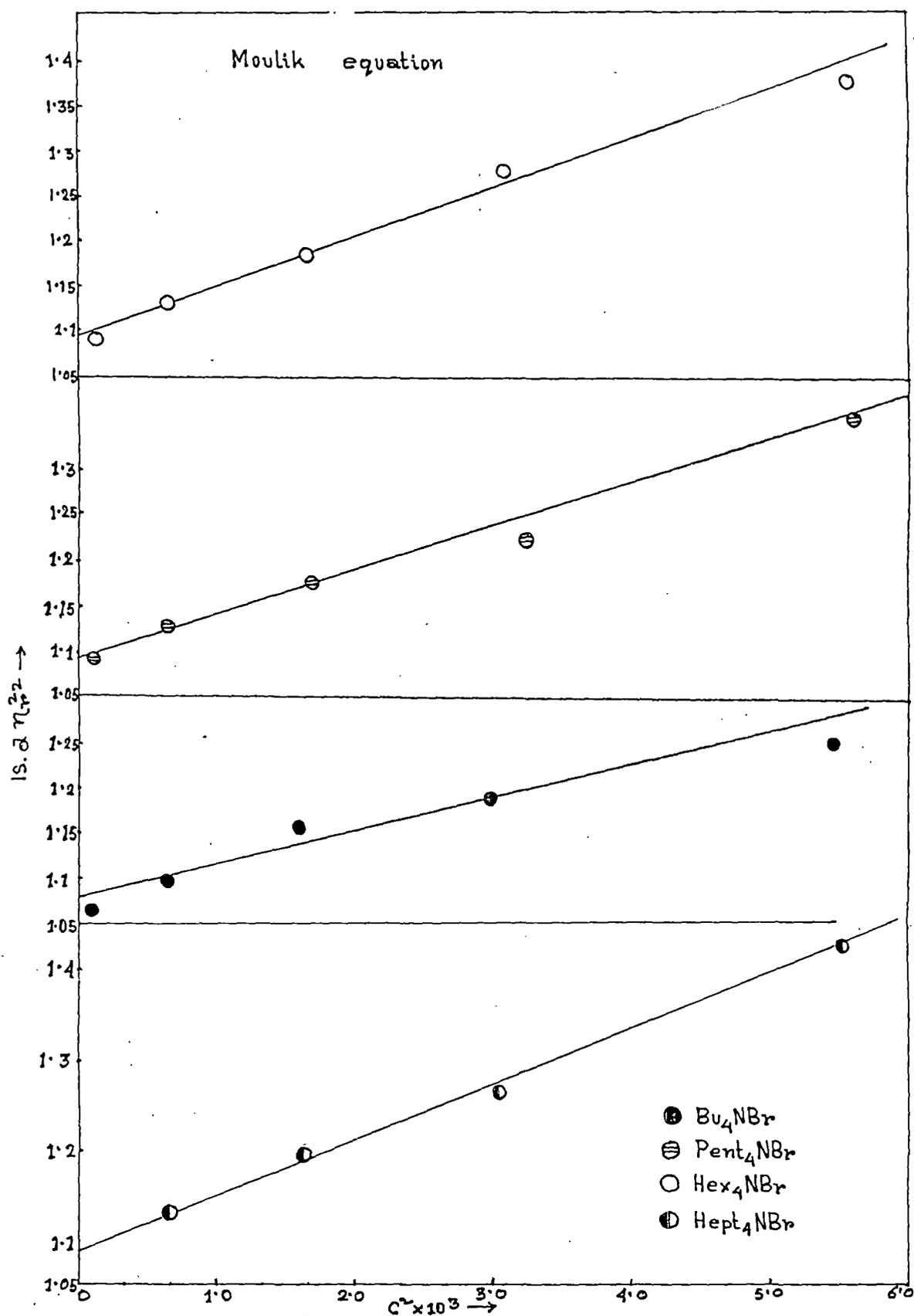


Fig-3 Plots of $(\eta_{sp})^2$ vs C^2 for different tetraalkylammonium bromides in THF at 25°C.

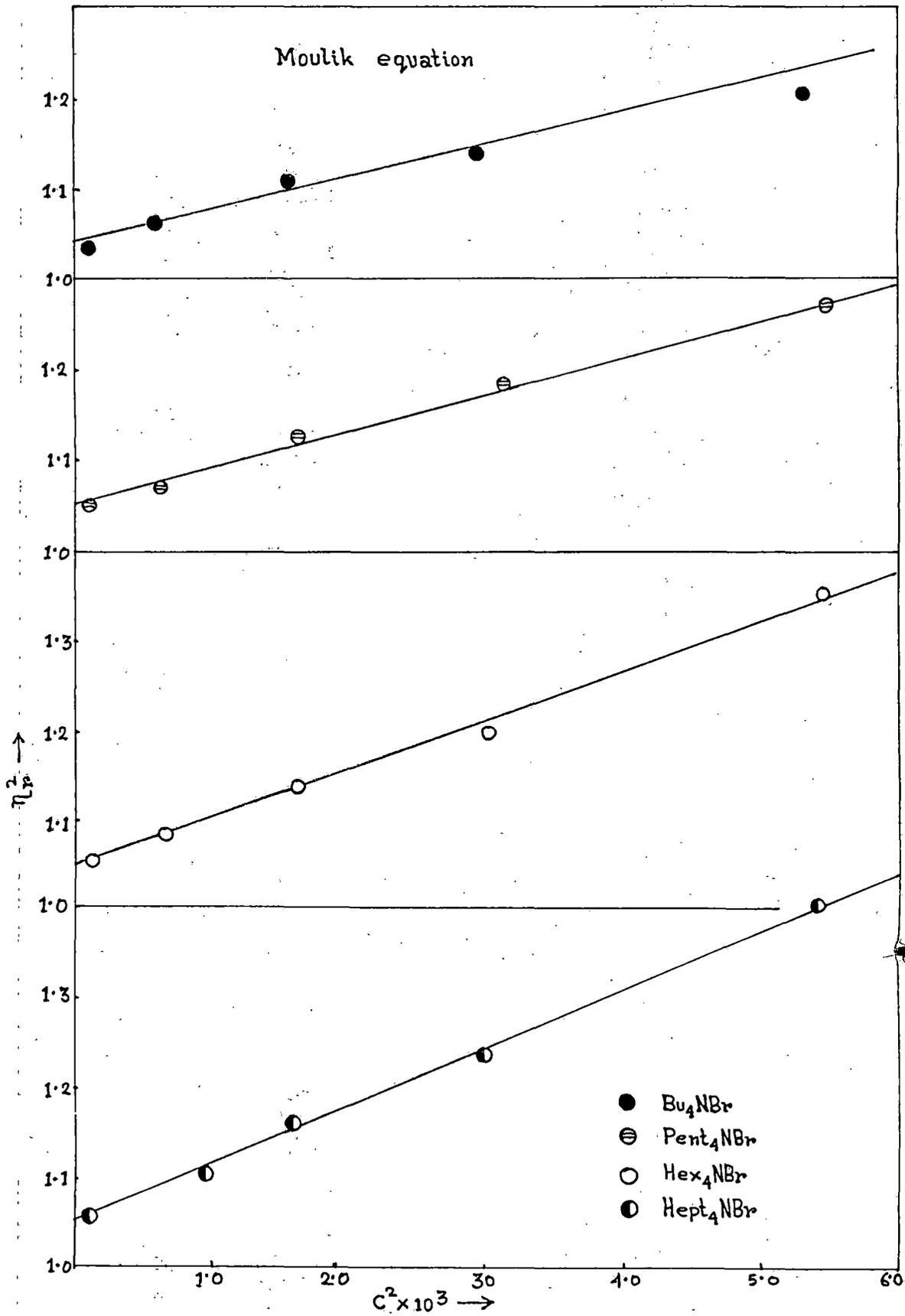


Fig-4 Plots of $(\eta_r)^2$ vs C^2 for different tetraalkylammonium bromides in THF at 35°C.

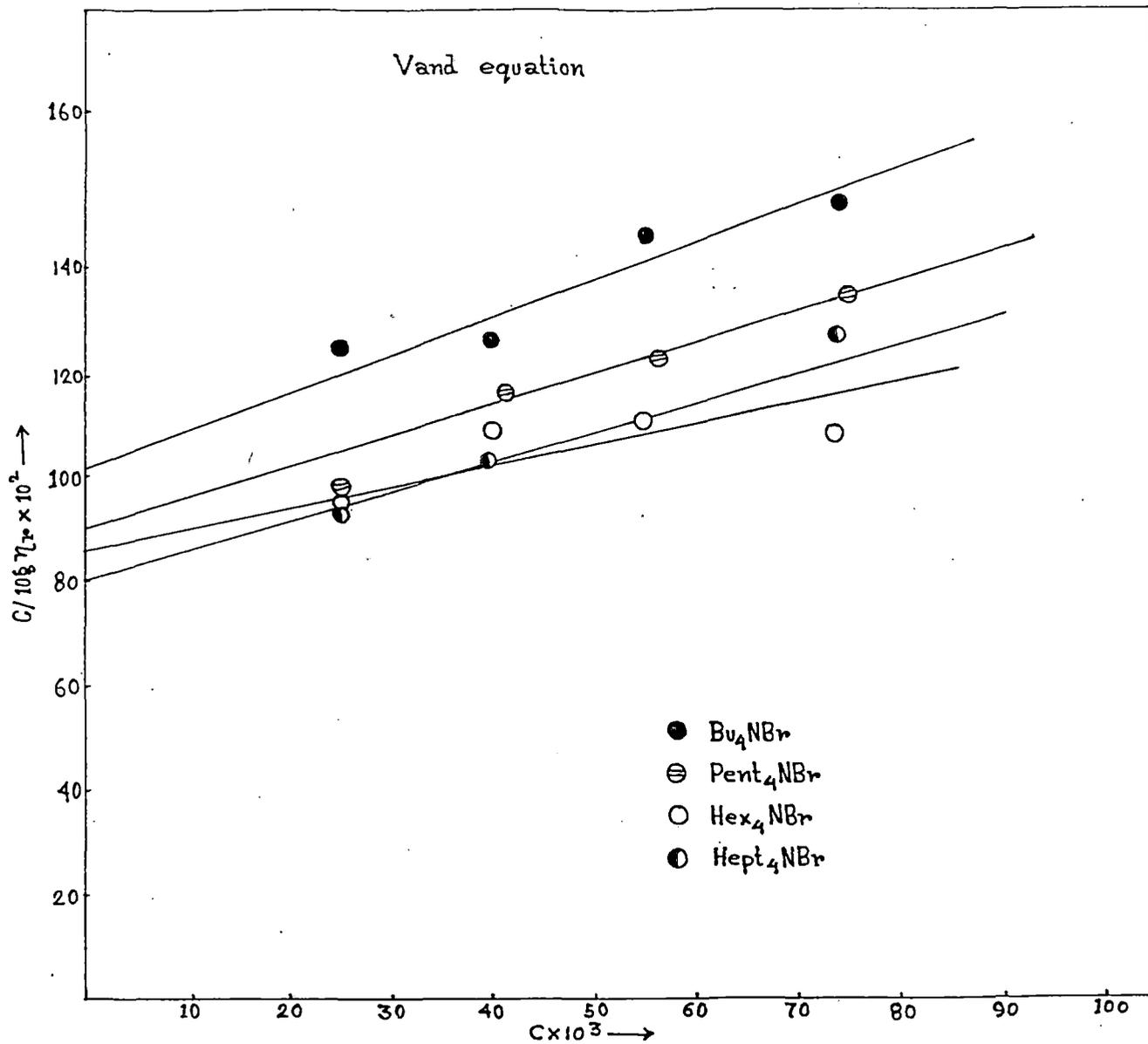


Fig-5 Plots of $C/10^5 \eta_{sp}$ vs C for different tetraalkylammonium bromides in THF at 25° C