

# Studies on Surface Tension and Parachor of Copper Soap Solutions in Nonaqueous Solvents

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## Abstract

Colloid chemical behavior of copper soaps in nonaqueous solvents has been investigated from the surface tension results using Szyszkowski's empirical equation:  $\gamma = \gamma_0 (1 + X \ln Y) - X \gamma_0 \ln C$ . The parachors of the soap solutions in hydrocarbons are independent of the soap concentration. However, in alcohols these values increase with the increase of soap concentration. Hammic and Andrew's mixture law equation has been successfully applied to explain the behavior in alcoholic soap solutions.

## Introduction

In a previous communication (Mehrotra et al., personal communication) the critical micelle concentration (cmc) for copper soap solutions in organic solvents was determined from various physical properties. The dispersion state of copper (II) soaps in nonaqueous solvents has been investigated from the determination of magnetic susceptibility measurements (1).

In the present work the surface tension and parachor behavior of solutions of copper soaps (viz. caproate, caprylate and caprate) in hydrocarbons and alcohols have been investigated. Szyszkowski's (2) empirical equation has been used to show that the micelles formed in two groups of solvents are different.

## Experimental Procedures

The chemicals were purified and soaps prepared by the methods described in the previous communications (1,3).

The solutions of copper soaps were prepared by dissolving the required amount of the soaps in organic solvents. Care was taken to avoid small amounts of water which were found to hydrolyze the soap.

The surface tension and density of the soap solutions were determined by means of stalgmeter and pycnometer respectively in a thermostatically controlled bath at  $40 \pm 0.05$  C. The accuracy of the results was checked by measuring the surface tension of pure and dried benzene of analytical grade. The difference in the results was below 0.5%. The surface tension results are in dynes/cm.

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## Results and Discussion

The surface tension,  $\gamma$ , of the soap solutions in chloroform, benzene, chlorobenzene and xylene decreases whereas in propanol-1, butanol-1 and pentanol-1 it increases with the increase of soap concentration. The variation of the surface tension,  $\gamma$ , of soap solutions against logarithm of the soap concentration,  $\log C$ , is characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the cmc of the soap (Fig. 1 and 2).

It may be pointed out that the linear variation of the surface tension,  $\gamma$ , with the logarithm of soap concentration,  $\log C$ , is in agreement with Szyszkowski's empirical equation for solutions of fatty acids:

$$\frac{\gamma}{\gamma_0} = 1 - X \ln \frac{C}{Y} \quad [1]$$

where  $\gamma$  and  $\gamma_0$  are the surface tensions of solutions of concentration  $C$  and of pure solvent, respectively and  $X$  and  $Y$  are constants. Equation 1 can also be written as:

$$\gamma = \gamma_0 [1 + X \ln Y] - X \gamma_0 \ln C \quad [2]$$

$$= I - X \gamma_0 \ln C \quad [3]$$

where constant  $I$  represents the intercept of the plots of  $\gamma$  against  $\log C$ .

The plots of  $\gamma$  against  $\log C$  for soap solutions are characterized by an intersection of two straight lines at the cmc. Therefore, the behavior of the soap solutions below and above the cmc may be represented by two linear equations. These equations have different values of the slopes and intercepts.

$$\gamma = I_1 - X_1 \gamma_0 \ln C \quad [4]$$

$$= I_2 - X_2 \gamma_0 \ln C \quad [5]$$

On differentiating Equations 4 and 5 we get:

$$\frac{d\gamma}{d \log C} = -2.303 X_1 \gamma_0 \equiv B_1 \quad [6]$$

and

$$\frac{d\gamma}{d \log C} = -2.303 X_2 \gamma_0 \equiv B_2 \quad [7]$$

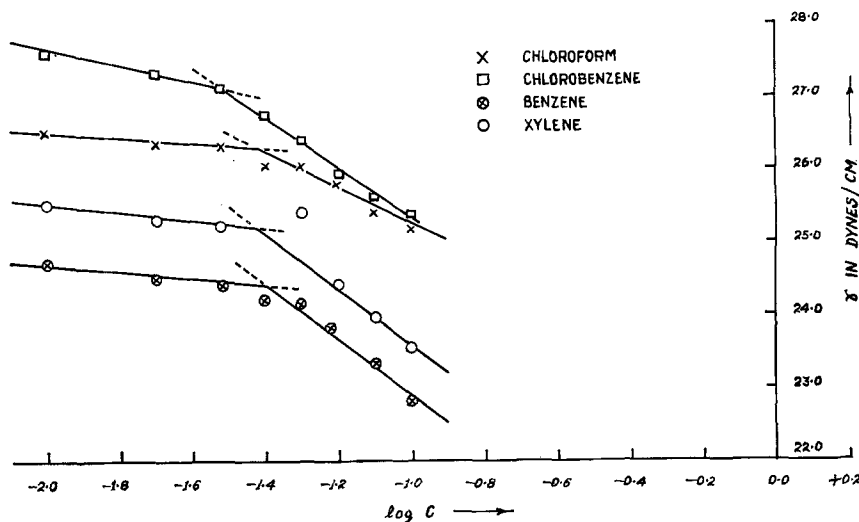


FIG. 1. Variation of surface tension,  $\gamma$ , of caproate solutions with  $\log C$ .

The values of the slopes,  $B_1$  and  $B_2$  and the intercepts  $I_1$  and  $I_2$ , of the plots of  $\gamma$  against  $\log C$  for various soap solutions in different solvents have been evaluated and are summarized in Tables I and II.

It is observed that the values of the intercepts for soap solutions in hydrocarbons below the cmc are higher than those for the solutions above the cmc. In alcohols the values are lower below the cmc than above the cmc. This difference may be due to the fact that the alcohols and hydrocarbons take quite different positions in the micelles.

TABLE I

Values of the Slopes  $B_1$  and  $B_2$  Below and Above the cmc in the Plots of  $\gamma$  vs.  $\log C$  for Copper Soap Solutions

Solvent	Caproate		Caprylate		Caprate	
	$B_1$	$B_2$	$B_1$	$B_2$	$B_1$	$B_2$
Chloroform	0.30	2.70	1.00	2.50	1.50	3.00
Chlorobenzene	1.00	3.50	2.00	6.50	1.20	6.00
Benzene	0.50	3.60	2.00	3.00	1.00	3.50
Xylene	0.50	3.60	0.50	1.00	1.00	1.50
Propanol-1	0.20	0.60	0.20	0.60	0.20	0.65
Butanol-1	0.20	0.80	0.20	0.55	0.20	0.55
Pentanol-1	0.13	0.80	0.20	0.60	0.20	0.55

TABLE II

Values of the Intercepts  $I_1$  and  $I_2$  Below and Above the cmc in the Plots of  $\gamma$  vs.  $\log C$

Solvent	Caproate		Caprylate		Caprate	
	$I_1$	$I_2$	$I_1$	$I_2$	$I_1$	$I_2$
Chloroform	25.98	22.36	24.95	23.20	23.65	22.55
Chlorobenzene	25.58	21.64	27.20	24.65	28.10	25.40
Benzene	23.82	19.30	23.30	22.60	25.00	23.60
Xylene	24.54	19.00	24.20	23.85	24.50	23.80
Propanol-1	22.21	22.76	22.21	22.73	22.20	22.74
Butanol-1	22.81	23.58	22.90	23.36	22.81	23.35
Pentanol-1	24.58	25.40	24.70	25.30	24.68	25.16

TABLE III

Range of the Area Covered by the Soap Micelle Formed From 1 g Mole of the Copper Soap Below and Above the cmc in Nonaqueous Solvents

Solvent	Area $\times 10^{-10} \text{ cm}^{-2}$	
	Below the cmc $A_1$	Above the cmc $A_2$
Chloroform	4.10-8.00	3.01-2.00
Chlorobenzene	6.01-12.02	4.19-6.01
Benzene	3.07-10.02	1.13-2.15
Xylene	3.00-7.55	0.92-1.72
Propanol-1	30.06	9.39
Butanol-1	30.06	8.97
Pentanol-1	31.38	8.71

It may also be pointed out that the values of the slopes  $B_1$  and  $B_2$  are higher for soap solutions in hydrocarbons than in alcohols. It is interesting to note that the values of the slopes for soap solutions in alcohols are independent of the chain length of the alcohol. Such consistency is not observed for soap solutions in hydrocarbons. This again confirms that alcohol and hydrocarbons occupy different positions in the soap micelles.

According to the Gibb's adsorption equation the adsorption excess,  $\tau$ , (i.e., the excess concentration of the solute per unit area of the surface) is found to be:

$$\tau = -\frac{1}{RT} \cdot \frac{d\gamma}{d \ln C} \quad [8]$$

TABLE IV

Values of the Parachor, P, for Copper Soap Solutions in Hydrocarbons

Concentration of soap solution, g moles/liter	Caproate	Caprylate	Caprate
Chloroform			
0.00	181.8	181.8	181.8
0.01	182.0	186.1	184.6
0.02	186.6	185.7	184.6
0.03	186.7	185.8	184.5
0.04	186.7	186.1	184.6
0.05	186.1	186.1	184.3
0.06	186.7	186.1	184.4
0.08	186.6	186.1	184.8
0.10	186.1	.....	.....
Chlorobenzene			
0.00	242.9	242.9	242.9
0.01	236.7	241.4	240.5
0.02	236.4	240.6	240.6
0.03	236.1	240.4	240.5
0.04	234.4	239.7	240.7
0.05	234.4	239.3	240.9
0.06	234.6	238.0	240.5
0.08	234.4	239.5	240.2
0.10	234.5	.....	.....
Benzene			
0.00	204.7	204.7	204.7
0.01	202.1	203.8	204.6
0.02	202.1	202.6	204.7
0.03	202.1	202.5	206.0
0.04	201.2	201.0	205.2
0.05	201.5	202.5	205.2
0.06	201.7	202.5	205.9
0.08	201.2	202.3	205.4
0.10	200.4	.....	.....
Xylene			
0.00	280.0	280.0	280.0
0.01	279.1	278.2	279.6
0.02	279.2	277.7	279.9
0.03	279.1	278.0	279.9
0.04	277.7	278.3	280.5
0.05	280.2	279.2	280.0
0.06	278.4	279.5	.....
0.08	277.5	279.2	.....
0.10	276.8	.....	.....

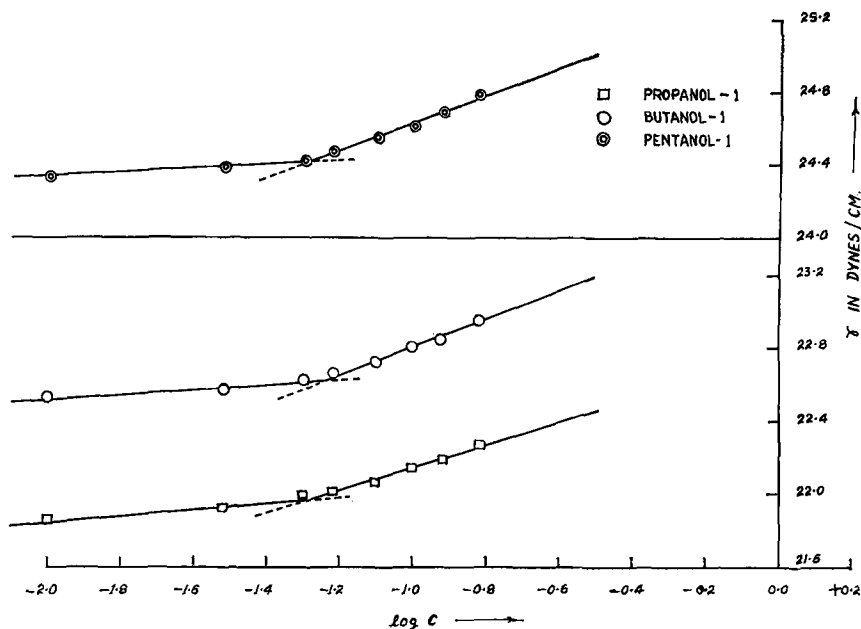


Fig. 2. Variation of surface tension,  $\gamma$ , of caproate in alcohols with  $\log C$ .

TABLE V  
Values of the Parachor, P, Mole Fraction, x and Constants k<sub>1</sub> and k<sub>2</sub> for  
Copper Soap Solutions in Alcohols

Concentration of soap solution, g mole/liter	x · 10 <sup>3</sup>	P = Vγ <sup>1/4</sup>	d(Vγ <sup>1/4</sup> )	(dx) · 10 <sup>3</sup>	k <sub>1</sub> Calculated	k <sub>1</sub> Graphically	k <sub>2</sub> Graphically
<b>Caproate</b>							
<b>Propanol-1</b>							
0.00	0.00	164.4	....	.....	.....		
0.01	0.75	163.9	....	.....	.....		
0.02	2.24	164.4	0.5	1.49	335.5		
0.03	3.75	165.1	1.2	2.99	401.3	430.7 I	163.8 I
0.05	4.48	165.4	1.5	3.78	402.1		
0.06	5.96	166.0	2.1	5.21	403.7		
0.08	7.44	166.5	2.6	6.69	397.6	400.0 II	163.3 II
0.10	8.92	167.1	3.2	8.17	391.6		
0.12	11.00	168.0	4.1	10.25	400.0		
<b>Butanol-1</b>							
0.00	0.00	201.5	....	.....	.....		
0.01	0.92	202.2	....	.....	.....		
0.03	2.74	202.9	0.7	1.82	384.6		
0.05	4.55	203.5	1.3	3.63	358.1	833.3 I	201.9 I
0.06	5.46	203.9	1.7	4.54	374.4		
0.08	7.27	204.6	2.4	6.35	377.9	444.4 II	201.0 II
0.10	9.06	205.6	3.4	8.14	417.8		
0.12	10.86	206.3	4.1	9.94	412.5		
0.15	18.53	206.7	4.5	12.61	356.9		
<b>Pentanol-1</b>							
0.00	0.00	242.4	....	.....	.....		
0.01	1.08	243.1	....	.....	.....		
0.03	3.24	243.8	0.7	2.16	324.1		
0.05	5.39	244.4	1.3	4.31	301.6	363.3 I	243.0 I
0.06	6.46	244.7	1.7	5.38	315.9		
0.08	8.60	245.7	2.4	7.52	319.2		
0.10	10.75	246.3	3.4	9.67	351.6	388.8 II	242.2 II
0.12	12.85	247.1	4.1	11.76	348.6		
0.15	16.01	247.5	4.5	15.93	285.5		
<b>Caprylate</b>							
<b>Propanol-1</b>							
0.00	0.00	164.4	....	.....	.....		
0.01	0.75	163.9	....	.....	.....		
0.02	1.50	164.2	0.3	0.75	400.0		
0.03	2.24	164.6	0.7	1.49	469.8	500.0 I	163.2 I
0.04	2.99	165.0	1.1	2.24	491.1		
0.05	3.75	165.5	1.6	2.99	535.1		
0.06	4.48	166.0	2.1	3.78	569.4		
0.08	5.96	166.5	2.6	5.21	499.1	512.0 II	163.9 II
0.10	7.44	167.5	3.6	6.69	539.5		
0.12	8.92	168.2	4.3	8.17	526.4		
<b>Butanol-1</b>							
0.00	0.00	201.5	....	.....	.....		
0.01	0.92	202.1	....	.....	.....		
0.02	1.83	202.5	0.4	0.91	439.6		
0.03	2.74	203.0	0.9	1.82	494.4	475.0 I	201.8 I
0.04	3.63	203.4	1.3	2.71	479.6		
0.05	4.55	203.9	1.8	3.63	496.0		
0.06	5.46	204.4	2.3	4.54	506.5		
0.08	7.27	205.3	3.2	6.35	503.9	545.4 II	201.2 II
0.10	9.06	206.3	4.2	8.14	514.7		
0.12	10.86	207.2	5.1	9.94	501.4		
<b>Pentanol-1</b>							
0.00	0.00	242.4	....	.....	.....		
0.01	1.08	242.9	....	.....	.....		
0.02	2.16	243.4	0.50	1.08	463.0		
0.03	3.24	244.0	1.10	2.16	521.1	583.3 I	242.0 I
0.04	4.32	244.4	1.50	3.24	463.0		
0.05	5.39	245.1	2.20	4.31	510.4		
0.06	6.46	245.3	2.40	5.38	446.1		
0.08	8.60	246.5	3.60	7.52	478.7	450.0 II	242.7 II
0.10	10.75	247.5	4.20	9.67	434.3		
0.12	12.84	248.5	5.10	11.76	433.7		
<b>Caprate</b>							
<b>Propanol-1</b>							
0.00	0.00	164.4	....	.....	.....		
0.01	0.75	163.5	....	.....	.....		
0.02	1.50	164.4	0.9	0.75	1200.0		
0.03	2.24	165.0	1.5	1.49	1007.0	875.0 I	163.0 I
0.04	2.99	165.5	2.0	2.24	892.0		
0.05	3.74	166.1	2.6	2.99	870.5		
0.06	4.48	166.5	3.0	3.73	804.2	633.0 II	163.9 II
0.08	5.96	167.4	3.9	5.21	748.7		
0.10	7.44	168.6	5.1	6.69	762.5		
<b>Butanol-1</b>							
0.00	0.00	201.5	....	.....	.....		
0.01	0.92	202.3	....	.....	.....		
0.02	1.83	202.8	0.5	0.91	549.5		
0.03	2.74	203.3	1.0	1.82	549.4	666.6 I	201.4 I
0.04	3.63	204.0	1.7	2.71	627.2		
0.05	4.55	204.6	2.3	3.63	648.5		
0.06	5.46	205.3	3.0	4.54	660.7	615.4 II	201.9 II
0.08	7.27	206.5	4.2	6.35	661.8		
0.10	9.06	207.6	5.2	8.14	638.9		
<b>Pentanol-1</b>							
0.00	0.00	242.4	....	.....	.....		
0.01	1.08	243.0	....	.....	.....		
0.02	2.16	243.8	0.8	1.08	740.8		
0.03	3.24	244.5	1.5	2.16	694.4	714.2 I	242.1 I
0.04	4.32	245.1	2.1	3.24	648.2		
0.05	5.39	246.0	3.0	4.31	696.0		
0.06	6.46	246.3	3.3	5.38	613.4	600.0 II	243.0 II
0.08	8.60	247.9	4.9	7.52	651.6		
0.10	10.75	249.2	6.2	9.67	641.2		

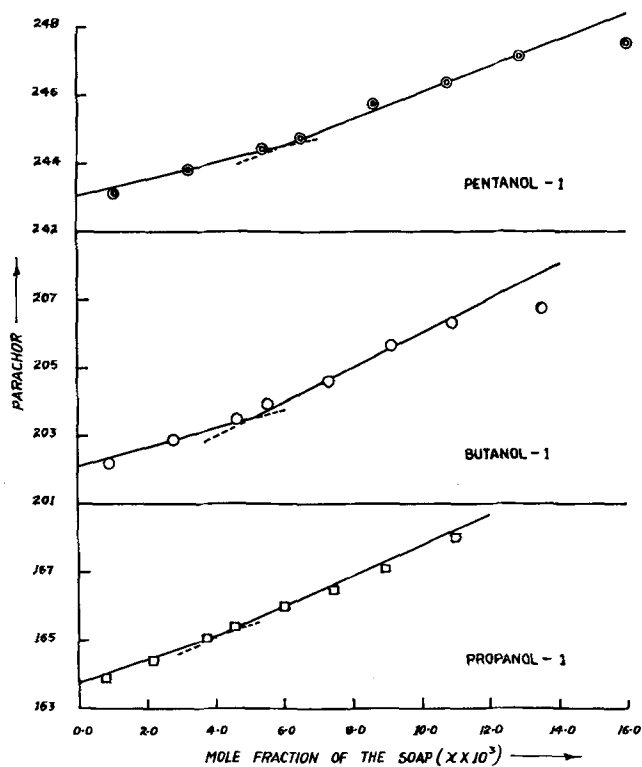


FIG. 3. Variations of parachor, of copper caproate solutions in alcohols with mole fraction of the soap.

By comparing Equation 8 with Equations 6 and 7 we get:

$$\tau_1 = \frac{X_1 \gamma_0}{RT} \text{ and } \tau_2 = \frac{X_2 \gamma_0}{RT} \quad [9]$$

Hence, the surface area covered by the soap micelles formed from 1 g mole of the soap below and above the cmc,  $A_1$  and  $A_2$ , can be represented as:

$$A_1 = \frac{RT}{X_1 \gamma_0} \text{ and } A_2 = \frac{RT}{X_2 \gamma_0} \quad [10]$$

The approximate values of the surface area occupied by the micelles formed by 1 g mole of the soap in alcohols is larger as compared to that in hydrocarbons (Table III). This may be ascribed to the fact that alcohols being polar solvents having a resultant dipole moment, exhibit a perturbing effect on the micelles due to the electric field; this leads to lesser aggregation of soap molecules. In hydrocarbons, due to their nonpolar nature, aggregation takes place to a greater extent. It is therefore concluded that the nature of the solvent plays a significant role in the micelle formation.

It may also be pointed out that the area occupied by 1 g mole of the soap below the cmc is larger as compared to that occupied by the soap micelles formed by the same amount of the soap above the cmc. This confirms that agglomeration of the soap molecules to form micelles results in the decrease in the surface area.

#### Parachor

The parachor,  $P$ , of the solution is written as:

$$P = \frac{M \gamma^{1/4}}{D} = V \cdot \gamma^{1/4} \quad [11]$$

where  $M$ ,  $D$ ,  $V$  and  $\gamma$  are respectively the molecular weight, density, molar volume and surface tension of the solution.

According to Hammie and Andrew's (4) mixture law equation, the parachor of the solution can be written as:

$$P = x P_{\text{soap}} + (1-x) P_{\text{solvent}} \quad [12]$$

where  $P$ ,  $P_{\text{soap}}$  and  $P_{\text{solvent}}$  refer to the parachors of the soap solution, soap and solvent respectively and  $x$  is the mole fraction of the soap in the solution.

TABLE VI  
Values of the cmc (g moles/liter) for Copper Soaps in Alcohols  
From Parachor Measurements

Solvent	Caproate	Caprylate	Caprate
Propanol-1	0.052	0.051	0.051
Butanol-1	0.056	0.052	0.043
Pentanol-1	0.054	0.045	0.045

Since  $P_{\text{soap}}$  and  $P_{\text{solvent}}$  are constants Equation 12 can be written as:

$$P = x [P_{\text{soap}} - P_{\text{solvent}}] + P_{\text{solvent}} = x k_1 + k_2 \quad [13]$$

where  $k_1$  is equal to  $(P_{\text{soap}} - P_{\text{solvent}})$  and  $k_2$  is equal to  $P_{\text{solvent}}$ . Hence from Equations 11 and 13 we have

$$P = V \gamma^{1/4} = x k_1 + k_2 \quad [14]$$

The equation shows that the plots of  $V \gamma^{1/4}$  against  $x$  should be linear.

On differentiating Equation 14 we get:

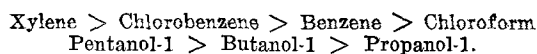
$$\frac{d(V \gamma^{1/4})}{dx} = k_1 \quad [15]$$

This shows that the quantity  $\frac{d(V \gamma^{1/4})}{dx}$  should be equal to  $k_1$ , i.e.,  $(P_{\text{soap}} - P_{\text{solvent}})$ .

The values of  $k_1$  have been calculated using Equation 15 for soap solutions in different alcohols and compared graphically by plotting  $P$  against  $x$ . The results are summarized in Table V.

It is observed that the parachors for soap solutions in hydrocarbons are fairly constant (Table IV). In alcohols however these values increase with the increase in the soap concentration (Table V). This further suggests that hydrocarbons and alcohols behave differently in the micelle formation.

It may be pointed out that the parachors of soap solutions in various solvents are in the order:



The difference in the values of the parachors in different solvents is mainly due to the difference in the parachors of pure solvents.

The values of the parachors,  $P$ , of soap solutions in alcohols have been plotted against mole fraction,  $x$ , of the soap (Fig. 3) to test the validity of Equation 14. It may be pointed out that the plots of the parachors against the mole fraction of soap are characterized by an intersection of two straight lines at a point which corresponds to the cmc of the soap (Table VI). This is in agreement with the values obtained earlier (Mehrotra et al., personal communication). This shows that soap exists in different forms below and above the cmc in alcoholic soap solutions. Therefore, parachor behavior may be represented by two linear equations having different values of the constants  $k_1$  and  $k_2$ .

It is noticed that the calculated values of  $k_1$  using Equation 15 are in close agreement with the values obtained graphically. This shows that there is justification in applying the above equations to the soap solutions in alcohols. The values of  $k_2$  (i.e., parachor of the solvent) obtained graphically are in close agreement with the experimental values of parachors of liquids used as solvents. Hence Hammie and Andrew's equation can be successfully applied to the soap solutions in alcohols.

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