Solubility and Refractometric Studies With Copper Valerate and Caproate in Nonaqueous Solutions

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Abstract

The behavior of copper valerate and caproate in nonaqueous solutions has been investigated from solubility and refractometric methods. The apparent heat of solutions demonstrate the existence of micellar aggregates above the Krafft point. The refractive indices of soap solutions in hydrocarbons decrease whereas in alcohols increase with the increase in the soap concentration.

Introduction

In an earlier communication we have investigated the diffuse reflectance spectra of copper (II) soaps in the solid state (1). We have established that the anomalously low magnetic moments of copper soaps corresponding to the binuclear structure persist in various organic solvents (2). The colloid chemical behavior of copper soaps in nonaqueous solutions has also been studied from the surface tension and parachor measurements (3).

In the present work the solubility of copper valerate and caproate provide evidence for the existence of miceller aggregates above the Krafft point in different organic solvents. The study of refractive index has been used to show that the micelles formed in two groups of solvents (hydrocarbons and alcohols) are different.

Experimental Procedures

The chemicals were purified, the soaps and the soap solutions prepared by the methods previously reported (2,4).

The solubility of copper (II) valerate and caproate was determined by the usual method of preparing a saturated solution of the soaps in different solvents at different temperatures and analyzing the clear supernatant liquid by weighing. The solutions attained equilibrium after a long time (5–7 hr).

An Abbe type refractometer (Bellingham and

TABLE I
Solubility of Copper Valerate and Caproate (g/100 g of solvent) in Nonaqueous Solvents

Temp. C	Chloro-benzene	Benzene	Xylene	Propanol-1	Butanol-1	Pentanol-1
20CV[a]	0.017	0.043	0.004	3.154	3.329	5.020
CC[b]	0.058	1.302	0.061	6.026	4.736	5.735
25CV	0.028	0.052	0.004	4.592	4.000	5.521
CC	0.068	1.640	0.075	6.398	5.008	8.509
30CV	0.033	0.063	0.004	7.386	4.960	6.512
CC	0.120	1.910	0.079	6.840	6.012	10.230
35CV	0.041	0.069	0.004	8.486	6.302	7.603
CC	0.553	3.810	0.084	11.320	8.337	13.190
40CV	0.128	0.178	0.011	12.490	9.572	12.620
CC	1.195	8.960	0.137	13.810	11.850	14.550
45CV	0.220	0.486	0.021	.....	.....	.....
CC	3.548	21.680	0.280	.....	.....	.....
50CV	0.380	1.830	0.038	.....	.....	.....
CC	12.030	26.300	1.160	.....	.....	.....

[a] Copper valerate.
[b] Copper caproate.

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TABLE II
Values of Apparent Heat of Solution (K cals/mole) for Copper Valerate and Caproate in Nonaqueous Solvents

Solvent	Copper valerate		Copper caproate	
	a[a]	b[b]	a	b
Chlorobenzene	44.12	6.52	43.12	17.38
Benzene	39.80	6.64	31.96	7.95
Xylene	60.00	.....	34.46	7.22
Propanol-1	16.56	13.20	19.33	2.34
Butanol-1	16.12	6.39	18.64	6.43
Pentanol-1	20.76	6.70	10.75	6.01

[a] a, Above the Krafft point.
[b] b, Below the Krafft point.

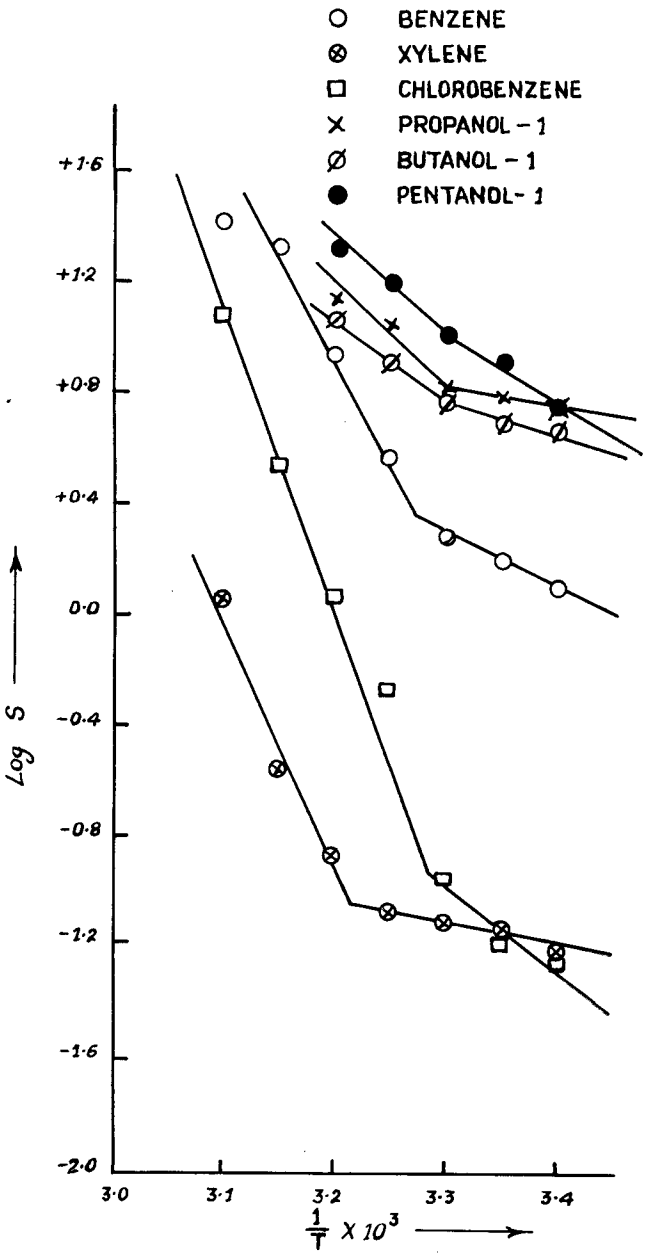

FIG. 1. Variation of log S with 1/T for caproate.

TABLE III
Values of Refractive Index for Copper Soap Solutions in Hydrocarbons

Concn. of soap solution g mole/liter	Chloroform		Chlorobenzene		Benzene		Xylene	
	CV[a]	CC[b]	CV	CC	CV	CC	CV	CC
0.00	1.4337	1.4337	1.5131	1.5131	1.4890	1.4890	1.4872	1.4872
0.01	1.4337	1.4337	1.5131	1.5131	1.4890	1.4890	1.4870	1.4870
0.02	1.4335	1.4336	1.5131	1.5131	1.4890	1.4890	1.4870	1.4870
0.03	1.4335	1.4335	1.5131	1.5131	1.4890	1.4890	.....	1.4870
0.04	1.4330	1.4333	1.5125	1.5124	1.4888	1.4883	.....	1.4868
0.05	1.4328	1.4330	1.5120	1.5120	1.4885	1.4880	.....	1.4862
0.06	1.4326	1.4328	1.5115	1.5115	1.4882	1.4878	.....	1.4862
0.08	1.4322	1.4322	.....	1.5106	1.4880	1.4873	.....	1.4855
0.10	1.4318	1.4320	.....	1.5098	1.4875	1.4868	.....	1.4852

[a] Copper valerate.
[b] Copper caproate.

Stanley Ltd., London) was used for measuring the refractive indices of soap solutions. All the measurements were made at a constant temperature (40 ± 0.05 C) by circulating the water from a thermostatically controlled bath. Sodium (D) line was used as a source of light and the refractometer was standardized from time to time with the help of a glass slab of known refractive index provided with the instrument. The density of the soap solutions was determined by means of pyknometer at the above mentioned temperature.

Results and Discussion

Solubility

The solubility-temperature curves of copper soaps in organic solvents (viz., chlorobenzene, benzene, xylene, propanol-1, butanol-1 and pentanol-1) are not exponential in nature but show a marked increase in the solubility in a small range of temperature indicating the existence of micellar aggregates above this temperature (Krafft point). The solubility method, therefore, gives one of the direct measure of micelle formation. The solubility data for copper valerate and caproate in different organic solvents at different temperatures are given in Table I. It is observed that the soaps have low solubility in hydrocarbons as compared to that in alcohols.

The plots of logS against 1/T are characterized by an intersection of two straight lines at a point which corresponds to the Krafft point (Fig. 1), pointing towards the existence of micellar aggregates above these temperatures for copper soaps. Micelles begin to form at 30 C in alcohols and 32–40 C in hydrocarbons.

The apparent heat of solution can be calculated from the Van't Hoff reaction isochore expression $d \log_e S/dT = Q/RT^2$ where S is the solubility in moles per liter and Q is the heat of solution. Assuming that Q is independent of temperature this expression yields, on integration,

$$\log_{10}S_2 - \log_{10}S_1 = \frac{Q(T_2 - T_1)}{2.303 \times 1.99 \times T_2T_1}$$

The average values of apparent heat of solution for valerate and caproate are summarized in Table II. The large difference in the values of heat of solution (above and below the Krafft point) confirms the formation of micelles in copper soap solutions in organic solvents. It is also observed that difference in the heat of solution is more marked in hydrocarbons than in alcohols. This supports the view that the tendency of micelle formation is more pronounced in hydrocarbons than in alcohols. It may also be con-

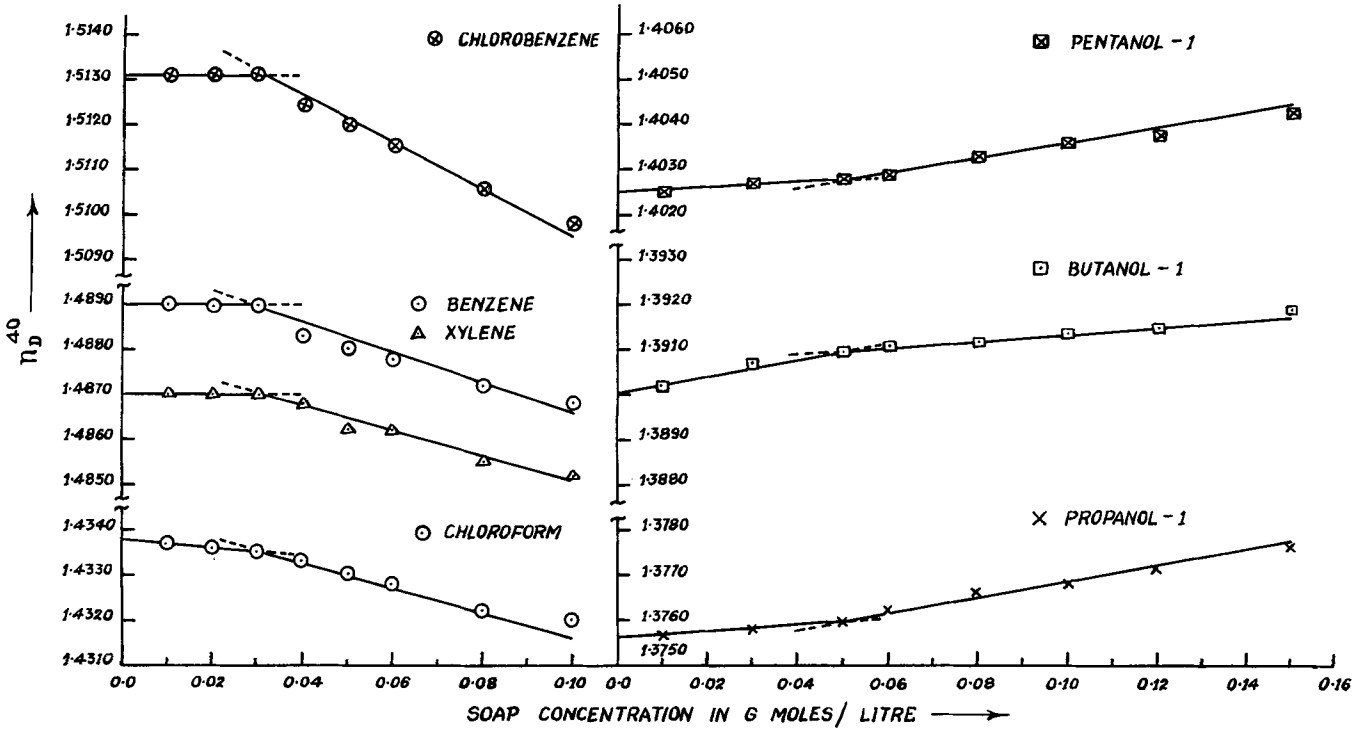

FIG. 2. Variation of refractive index of caproate solutions with soap concentration.

TABLE IV
Values of Refractive Index for Copper Soap Solutions in Alcohols

Concn. of soap solution g mole/liter	Propanol-1		Butanol-1		Pentanol-1	
	CV[a]	CC[b]	CV	CC	CV	CC
0.00	1.3754	1.3754	1.3890	1.3890	1.4022	1.4022
0.01	1.3757	1.3757	1.3898	1.3902	1.4026	1.4025
0.03	1.3758	1.3758	1.3900	1.3907	1.4030	1.4027
0.05	1.3759	1.3760	1.3903	1.3910	1.4033	1.4028
0.06	1.3760	1.3762	1.3905	1.3911	1.4034	1.4029
0.08	1.3763	1.3766	1.3906	1.3912	1.4038	1.4033
0.10	1.3767	1.3768	1.3907	1.3914	1.4038	1.4036
0.12	1.3769	1.3771	1.3911	1.3915	1.4039	1.4038
0.15	1.3776	1.3776	1.3913	1.3919	1.4040	1.4043

[a] Copper valerate.
[b] Copper caproate.

cluded that the nature of the solvent plays significant role in the micelle formation.

Refractive Index

The refractive index, n, of soap solutions in chloroform, chlorobenzene, benzene and xylene at first remains almost constant and then decreases with the increase in the soap concentration (Table III). However, in propanol-1, butanol-1 and pentanol-1 it increases with the increase in the soap concentration (Table IV). The difference in the behavior of soap solutions in alcohols and hydrocarbons may be due to the fact that these solvents take quite different positions in the soap micelles.

The plots of the refractive index, n, of soap solution as a function of concentration, c, are characterized by an intersection of two straight lines at a point corresponding to the critical micelle concentration (cmc) of the soap (Fig. 2), in agreement with the values obtained earlier (Mehrotra et al., personal communication).

TABLE V
Values of the cmc (g moles/liter) for Copper Valerate and Caproate in Nonaqueous Solvents From Refractive Index Measurements

Solvent	Copper valerate	Copper caproate
Chloroform	0.028	0.030
Chlorobenzene	0.027	0.033
Benzene	0.027	0.029
Xylene	.....	0.031
Propanol-1	0.050	0.055
Butanol-1	0.065	0.054
Pentanol-1	0.064	0.050

It may be pointed out that the values of the cmc (Table V) of the soaps in alcohols are higher than those in hydrocarbons. This difference demonstrates clearly that the agglomeration of soap molecules takes place at a lower soap concentration in hydrocarbons as compared to that in alcohols.

The refractive indices of soap solutions in the various solvents are in the order: chlorobenzene > benzene > xylene > chloroform, and pentanol-1 > butanol-1 > propanol-1.

The difference in the refractive indices of soap solutions in various solvents is mainly due to the difference in the refractive indices of pure solvents.

It is observed that the extrapolated values of the refractive index, for zero soap concentration, n_o, for soap solutions in hydrocarbons is in complete agreement with the refractive indices of pure solvents. The values in alcohols are slightly higher than the refractive indices of pure alcohols used as solvents. This difference confirms that the micelles formed in the two groups of solvents are different.

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