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Influence of Methyl, Ethyl, Propyl & *n*-Butyl Alcohols on the Stability of Oil-Water Emulsions

M. K. SHARMA, S. K. JHA & S. N. SRIVASTAVA
Department of Chemistry, Agra College, Agra 282002

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The effect of methyl, ethyl, propyl and *n*-butyl alcohols on sodium benzylpenicillin- and chloramphenicol-stabilized oil-water emulsions has been studied by measuring the zeta-potentials microelectrophoretically. In general, the zeta-potential decreases with increasing percentage of alcohols. However, for the chloramphenicol-stabilized emulsions there is a slight increase in zeta-potential in the initial stages. The changes in zeta-potential due to the addition of KNO_3 in the presence of different amount of alcohols have also been examined, and the order of flocculation concentration of KNO_3 has been found to be *n*-butanol$<$propanol$<$ethanol $<$methanol. The order of effectiveness of alcohols in bringing about a decrease in zeta-potential is *n*-butanol$>$propanol$>$ethanol$>$methanol.

ALTHOUGH quite a few references are available[1-6] on the studies of the interaction of non-electrolytes on colloidal sols, in general, data on the behaviour of emulsions in the presence of non-electrolytes are rather sparse. Some workers[7-10] have studied the sensitization effect and the adsorption of some alcohols on Fe_2O_3, AS_2O_3, $Fe(OH)_3$ and other sols. Ghosh and Dhar[11] have reported the sensitization effect of sugar on As_2O_3 sol, while Mukherjee and Chaudhury[12] observed a decrease in the cataphoretic velocity when sugar was added to the sol and an increase in chemical adsorption. Mukherjee[13] also measured the cataphoretic velocity in the presence of ethanol, sugar and some electrolytes, and the results were explained on the basis of a double layer.

In the present paper are reported the results of studies on the interaction of some alcohols such as methanol, ethanol, propanol and *n*-butanol on the oil-water emulsions stabilized by sodium benzylpenicillin or chloramphenicol. Besides the changes in the properties of the dispersion medium an attempt has been made to explain the decrease in zeta-potential and its variation with different alcohols on the basis of adsorption of alcohol molecules at the surface of the oil globules.

Materials and Methods

Pure samples of sodium benzylpenicillin (Alembic Chemical grade) and chloramphenicol (Parke Davis grade) were used. The alcohols and other chemicals used were of Analar BDH grade.

Emulsions were prepared by dispersing 2% by volume of toluene or xylene in aq. solution of sodium benzylpenicillin and chloramphenicol separately. Toluene was made heavier by adding chloroform. This has been practised in similar systems to avoid creaming[14]. The final mixture also contained $0{\cdot}01M$ KCl. The mixture was shaken for 30 min and finally homogenized in a stainless steel homogenizer (Fisher Scientific Co., USA). In all the estimations emulsions were prepared and sampled under identical conditions so as to have maximum precision.

The electrophoretic mobilities of the emulsion-globules were measured microelectrophoretically using a Northrop-Kunitz[15] type flat rectangular cell fitted in a specially designed apparatus. The diluted emulsion was filled in the cell and the electrode chambers were filled with an equiconducting potassium chloride solution to avoid diffusion. A constant dc voltage was applied across the two silver-silver chloride electrodes.

The potential gradient was measured by recording the potential difference between the two platinized-platinum electrodes fused at both the ends of the cell chamber and so encased that only thier tips protruded into the cell chamber. Potentials were measured with the help of a vacuum tube voltmeter (model major, Electronic Products, India) using 12 AU_7 and 6 AL_5 vacuum tubes and having impendence of 11 MΩ on all ranges. The distance between these electrodes was measured directly with the help of a travelling microscope.

The velocity of the particles, as observed through microscope, was timed for 3-5 divisions of the graticule (1 div. $=0{\cdot}10\ \mu$) calibrated against a 1·0 mm standard micrometer scale divided to 0·01 mm.

Knowing the potential gradient (E) and velocity (V) of the globules, the electrophoretic mobility (U) was calculated using the relation

$$U=V/E \qquad \ldots(1)$$

Thus with the help of electrophoretic mobility, zeta-potential of the system was calculated using Helmholtz[16] equation which is applicable to the systems of spherical particles and $\varkappa a \gg 1$.

Results and Discussion

Effect of alcohols on zeta-potential — From Table 1 it is evident that for sodium benzylpenicillin-

TABLE 1 — ZETA-POTENTIALS AND MOBILITIES AS FUNCTION OF ALCOHOL PERCENTAGE

Alcohol %	A		B	
	$U \times 10^4$ (cm sec^{-1} V^{-1})	ζ (mV)	$U \times 10^4$ (cm sec^{-1} V^{-1})	ζ (mV)
	METHANOL			
2·5	4·44	71·93	4·05	65·61
5·0	4·09	66·28	4·16	67·39
8·0	3·76	60·91	3·96	64·15
10·0	3·47	56·21	3·73	60·42
15·0	2·72	44·06	3·11	50·38
17·5	—	—	2·79	45·20
20·0	2·50	40·50	2·64	42·77
25·0	—	—	2·39	38·72
30·0	2·35	38·07	2·30	37·26
	ETHANOL			
2·5	4·32	69·98	4·00	64·80
5·0	3·92	63·83	4·08	66·09
8·0	3·42	55·40	3·74	60·58
10·0	3·21	52·00	3·45	55·89
12·5	—	—	3·19	51·67
15·0	2·62	42·44	2·86	46·33
20·0	2·41	39·04	2·49	37·26
25·0	2·23	36·13	—	—
35·0	2·05	33·21	2·08	33·69
	PROPANOL			
1·5	4·33	70·15	3·92	60·50
2·5	4·13	66·90	3·83	62·05
5·0	3·69	59·78	3·62	58·64
10·0	2·96	47·95	3·11	50·38
15·0	2·44	39·53	2·55	41·31
20·0	2·26	36·61	2·21	35·80
22·5	—	—	2·08	33·69
25·0	2·10	34·02	1·97	31·91
	n-BUTANOL			
1·0	4·34	70·30	3·93	63·66
2·0	4·09	66·26	—	—
2·5	—	—	3·72	60·26
5·0	3·61	58·48	3·40	55·08
7·5	3·20	51·84	3·09	50·05
10·0	2·67	43·25	2·85	46·17
12·5	2·22	35·96	2·60	42·12
15·0	1·74	28·19	2·39	38·71
17·5	—	—	2·15	34·83
20·0	1·47	23·81	1·95	31·59
25·0	1·32	21·38	1·66	26·87

A = sodium benzylpenicillin-stabilized emulsion; and B = chloramphenicol-stabilized emulsion.

stabilized emulsions zeta-potential decreases sharply up to nearly 15% of alcohol concentration followed by a small but gradual decrease on further addition of alcohol with a clear tendency of approaching a limiting value. The magnitude of decrease in zeta-potential was greater in the case of higher alcohol. Thus percentage of an alcohol required for getting the same magnitude of decrease in zeta-potential was greater for the lower alcohol. The order of effectiveness has been found to be *n*-butanol>propanol>ethanol>methanol.

For chloramphenicol-stabilized emulsions there was a slight increase in zeta-potential on the addition

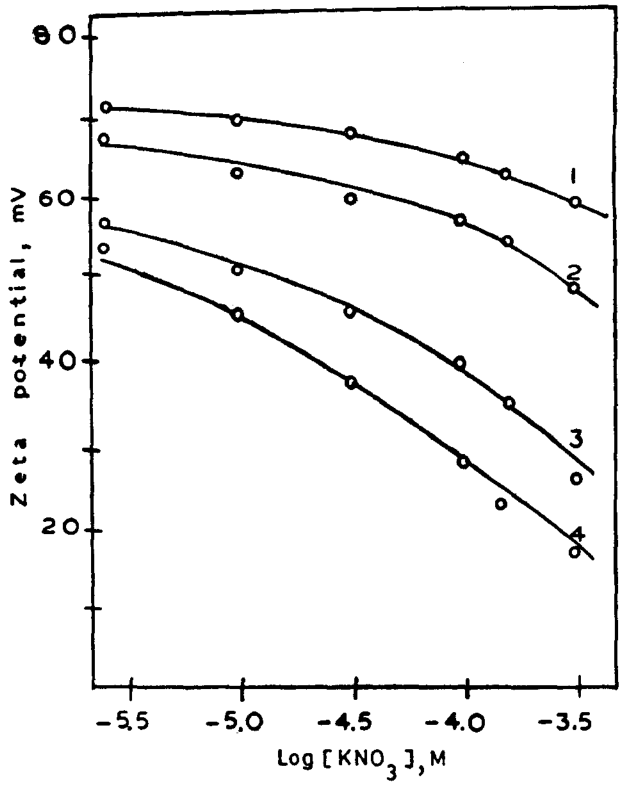

Fig. 1 — Variation of zeta-potential with [KNO_3] in the presence of methanol for sodium benzylpenicillin-stabilized emulsion [(1) 5%, (2) 10%, (3) 15% and (4) 20% MeOH]

of small amounts of methyl and ethyl alcohols (Table 1). This initial increase may be attributed to the surface conductance effect. Further increase in the percentage of alcohols lowered the zeta-potentials as stated above.

The alcohols with dielectric constant lower than that of water $\epsilon_{CH_3OH}=33$, $\epsilon_{C_2H_5OH}=24$, $\epsilon_{C_3H_7OH}=18{\cdot}3$, $\epsilon_{C_4H_9OH}=17$ and $\epsilon_{H_2O}=78{\cdot}5$) should increase the interionic attraction in their aq. mixtures. The increase in interionic attraction can affect the existence of free polar heads (the hydrophilic end of the micelle which is so vital for oil-water emulsion stability) because it is likely to suppress the ionization of ionic emulsifiers. Further, likelihood of ion-pair formation is increased and the polar heads forming the micelle are likely to be surrounded by ions (from KCl added in the preparation of the emulsion and the ionization of emulsifiers) of the opposite charge. These factors are thus likely to decrease the emulsifying activity of both the emulsifiers with increasing alcohol content in the aq. mixtures and with the length of the carbon chain for a given percentage of different alcohols because dielectric constants are in the reverse order of the chain length.

The increase in interionic attraction should produce reduction in zeta-potential and stability of the oil globules. In addition to this, as the concentration of an alcohol is increased, its adsorption at the surface of the oil-globules increases, the adsorption being greater the longer the carbon chain in the alcohol molecule. With increase in adsorption of an alcohol the number of molecules of the emulsifier squeezed out of the surface of the oil-globules increases and so the zeta-potential is lowered further.

Effect of electrolytes on zeta-potential in the presence of alcohols — The variation in zeta-potential due to the addition of KNO_3 in the presence of methyl alcohol is shown in Fig. 1. The nature of the curves in the presence of othe· alcohols is identical to that obtained in the case of methyl alcohol. The decrease in dielectric constant favours attraction between the oppositely charged species. Thus addition of alcohols should bring about an increase in attraction forces between the charged sites on the surface of the emulsion globules and oppositely charged ions in the solution, i.e. K^+ in the present case. The higher the alcohol greater will be this attraction. This explains the following order of flocculation concentration of KNO_3: *n*-butanol < propanol < ethanol < methanol.

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