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EFFECT OF DYES ON THE CRYSTAL HABIT AND OPTICS OF NaF, LiF, NaCl, KCl, KBr AND KI

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CONTENTS

ABSTRACT

The effect of 112 dyes on the crystal habit and optics of NaF, LiF, NaCl, KCl, KBr and KI was investigated experimentally. A few dyes are adsorbed on {111} and cause variation from the ordinary cubical habit to octahedral. Most dyes are adsorbed, if at all, by {100}. Habit variation is favored by a slow rate of growth of the crystals.

The nature of the adsorption mechanism is obscure. Adsorption control by the substitutional attachment of polar groups in the dye molecule into the structure of the adsorbing crystal, of the nature found by Buckley for the adsorption of dyes by oxysalts, appears from structural considerations to be very improbable. Dye adsorption mechanisms of the types described by Kolthoff and by Verwey for AgCl also appear to be inadequate to account for the observed effects. France's theory of adsorption by charged planes is found to be largely at variance with observation, and the theory itself is shown to be subject to a

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* The experimental work described herein was done at the Massachusetts Institute of Technology, Cambridge, Mass.

restriction which denies any application to the growth and adsorption phenomena of macroscopic crystals.

Many instances of anomalous pleochroism were observed. No connection was found between the occurrence of pleochroism and habit variation, nor could either of these effects be identified with special characters of the dyes concerned. Dyes have a marked skeletonizing effect on crystals of NaF and LiF. The effect is lacking with the alkali chlorides, bromides and iodides. Strong adsorption of dye, as evidenced by habit variation or a special skeletonizing effect, is accompanied by a tendency for supersaturation in the crystallizing solution.

INTRODUCTION

Crystals may change their habit and become colored and sometimes pleochroic when grown from solutions to which a dye has been added. Particular mention may be made of the pioneer work in this field by de Senarmont, in 1854, and of the recent studies by Gaubert, France and co-workers, and Buckley. A list of substances on which the effect of dyes has been investigated is given in Table 1. Extended reviews of the work with dyes, in correlation with other crystal-adsorption and crystal-orientation phenomena relevant to the subject of anomalous mixed crystals, have been given by Spangenberg and Neuhaus (1) and by Seifert (2).

The present paper deals with the effect of dyes on the habit and optics of NaF and other alkali halides of the NaCl structural-type. The influence of inorganic cosolutes and of organic cosolutes aside from dyes on NaF and other halides is described in an accompanying paper.

Description of Experimental Methods

Two different methods of crystallization were employed. With NaF, NaCl and LiF, 100 to 300 cc. of the dye-containing solution were evaporated at 80° to about half the original volume. The evaporation was usually so arranged as to take from 20 to 36 hours. Glass wool was added to the solutions to permit crystals to develop freely suspended in the solution.

Crystallization from large volume was found unsuited to KCl, KBr and KI, because of "creeping" and temperature-solubility effects noted below, and recourse was made to crystallization on microscope slides. The following technique was used. The dye was dissolved in a drop of water contained in a small beaker and 10 cc. of hot saturated alkali halide solution added thereto. A large deep drop of this solution was then formed on a hot microscope slide, and crystallization followed under the microscope. Crystals appear and grow with great rapidity, due to the marked change in solubility with temperature. The drop when cooled to room temperature consists of a slushy mass of crystals. This slush was then raked to one side, and a clear portion of the drop allowed to crystal-

TABLE 1. INDEX TO LITERATURE OF DYE-CRYSTAL SYSTEMS

Crystallized substance	Reference
AgBr	54
AgCl	54, 57
$Ba(NO_3)_2$	13, 14, 17, 22, 23, 36, 55, 68
$BaSO_4$	53
$BaCl_2 \cdot 2H_2O$	68
$CaCO_3$	56, 66
$CaC_2O_4 \cdot H_2O$	68
$CaSO_4 \cdot 2H_2O$	12, 24, 46
Cs alum	20
$CuSO_4 \cdot 5H_2O$	28, 33
$H_3AsO_4 \cdot \frac{1}{2}H_2O$	67
K alum	16, 19, 20, 21, 31, 34, 36, 38, 68
KBr	68
$KBrO_3$	68
KCl	4, 55, 68
$KClO_4$	54, 70, 73
$KClO_3$	16, 54, 68, 69, 74
KH_2PO_4	68
KI	68
KIO_3	68
KNa tartrate	2, 16
KNO_3	2, 68
K_2SO_4	52, 55, 58, 59, 68, 69, 70, 71, 72, 81
$MgCl_2 \cdot 6H_2O$	68
$MgNH_4$ sulphate	68
$MgSO_4 \cdot 10H_2O$	68
$Na_2B_4O_7 \cdot 10H_2O$	2, 68
NaBr	68
$NaBr \cdot 2H_2O$	68
NaCl	1, 55, 64, 68
$NaClO_3$	8, 16, 68, 75
NaF	64
$Na_2HPO_4 \cdot 12H_2O$	68
$NaI \cdot 2H_2O$	68
$NaNO_3$	2, 18, 68
Na_2SO_4	68
$Na_2SO_4 \cdot 10H_2O$	68
$Na_2S_2O_3 \cdot 5H_2O$	68
Na tartrate	25, 76
NH_4Br	1, 68
NH_4Cl	1, 68
NH_4ClO_4	54
$(NH_4)_2HPO_4$	26
$NH_4H_2PO_4$	68
NH_4H malate	25, 76
NH_4NO_3	68
$(NH_4)_2SO_4$	68
NH_4 tartrate	25, 76
$Pb(NO_3)_2$	13, 17, 22, 23, 27, 31, 36, 39, 43, 48, 49, 55, 68
RbH malate	25
$Sr(NO_3)_2$	13, 14, 23, 55, 68
$Sr(NO_3)_2 \cdot 4H_2O$	2, 3, 15, 28, 30, 32, 68
TlH malate	26
Tl_2SO_4	28
$ZnCl_2 \cdot H_2O$	28
$ZnSO_4 \cdot 7H_2O$	16, 68
Acetanilid	60
Alkaloid tartrates	76
Asparagine	76
Anilic acid	50
Benzoin	50, 60
Benzamid	60
Benzophenone	60, 62
Bromnitrobenzene	60
Chlornitrobenzene	62
Cinchonamine	62
Cinchone tartrate	76
Cinnamic acid	61
Codeine	62
Dibromobenzene	62
Dinitrobenzene	60
Erythritol	51
Formanilid	60
Haematoxylin	50
Helenine	80
Hippuric acid	50
Liquid crystals, etc.	25, 40, 41, 77
Maleic acid	50
Meconic acid	37, 47, 50
Mesaconic acid	50
Metaoxybenzoic acid	61
Morphine	28
Naphthalene	82

Table 1. Index to Literature of Dye-Crystal Systems—*Continued*

Crystallized substance	Reference	Crystallized substance	Reference
Narceine	9, 50	Succinamid	50
Oxalic acid	16, 42, 61	Succinic acid	50, 61
Papaverine	50	Sugar	2, 9
Paraoxybenzoic acid	61	Sulphonal	62
Phlorizin	6, 7, 47	Terpinol	62
Phthalic acid	11, 29, 45, 47, 50, 61,	Tetrachlorobenzene	62
	68	Thiourea	50
Phloroglucinol	78	Thymol	10
Picric acid	49	Trional	62
Piperonal	62	Urea nitrate	5, 12, 44, 47, 49
Protocatechuic acid	50, 61	Urea oxalate	5, 47, 49
Quinine sulphate	50	Uric acid	79
Salol	60	Vanillin	51, 62, 80
Strychnine tartrate	76	Veratric acid	50

1. Gaubert: *Bull. soc. min.*, **38,** 170, 176, 179 (1915). 2. de Senarmont: *Ann. chim. phys.*, **41,** 319 (1854). 3. Bertin: *Zeits. Krist.*, **3,** 454 (1878). 4. Claasen: *Am. J. Sc.*, **23,** 323 (1882). 5. Gaubert: *Compt. rend.*, **192,** 965 (1931). 6. Gaubert: *Compt. rend.*, **196,** 554 (1933). 7. Gaubert: *Compt. rend.*, **196,** 942 (1933). 8. Buckley: *Zeits. Krist.*, **75,** 15 (1930). 9. Ambronn: *Ber. deutsch. bot. Ges.*, **7,** 113 (1889). 10. Gaubert: *Bull. soc. min.*, **27,** 233 (1904). 11. Gaubert: *Bull. soc. min.*, **28,** 286 (1905). 12. Gaubert: *Bull. soc. min.*, **25,** 244 (1903). 13. Gaubert: *Bull. soc. min.*, **23,** 211 (1900). 14. Gaubert: *Bull. soc. min.*, **17,** 121 (1894). 15. Rosenbusch: *Mikro. Physiog. der Mineralien*, 1st ed., 106 (1873). 16. Milligan: *J. Phys. Chem.*, **33,** 1363 (1929). 17. Davis and France: *J. Phys. Chem.*, **45,** 81 (1936). 18. Weinland and France: *J. Phys. Chem.*, **36,** 2832 (1932). 19. Foote, Blake and France: *J. Phys. Chem.*, **34,** 2236 (1930). 20. Lash and France: *J. Phys. Chem.*, **34,** 724 (1930). 21. Buckley: *Zeits. Krist.*, **73,** 443 (1930). 22. Buckley: *Zeits. Krist.*, **76,** 147 (1930). 23. Walcott: *Am. Mineral.*, **11,** 221, 259 (1926). 24. Maschke and Vater: *Zeits. Krist.*, **33,** 57 (1900). 25. Gaubert: *Compt. rend.*, **167,** 368 (1918). 26. Seherr-Thoss: *Ann. Phys.*, **6,** 285 (1879). 27. Johnsen: *Jb. Min.*, II, 93 (1903). 28. Gaubert: *Bull. soc. min.*, **28,** 180 (1905). 29. Gaubert: *Compt. rend.*, **142,** 219 (1906). 30. Becquerel: *Ann. chim. phys.*, **14,** 249 (1888). 31. France: *Coll. Symp. Ann.*, **7,** 59 (1930). 32. Pelikan: *Tsch. Min. Mitth.*, **13,** 258 (1892). 33. Eckert and France: *J. Am. Ceramic Soc.*, **10,** 579 (1927). 34. Keenan and France: *J. Am. Ceramic Soc.*, **10,** 821 (1927). 35. Bennett and France: *J. Am. Ceramic Soc.*, **11,** 571 (1928). 36. France and Davis: *J. Phys. Chem.*, **40,** 177 (1936). 37. Gaubert: *Compt. rend.*, **151,** 1134 (1910). 38. Paine and Davis: *J. Phys. Chem.*, **39,** 425 (1935). 39. Gaubert: *Ann. Rpt. Smithson. Inst. for 1909*, 29 (1910). 40. Lehmann: *Ann. Phys.*, **2,** 682 (1900). 41. Lehmann: *Ann. Phys.*, **8,** 908 (1902). 42. Billiet: *Natuurw. Tijdschr.*, **15,** 52 (1933). 43. Nothaft and Steinmetz: *Chemie der Erde*, **5,** 225 (1930). 44. Gaubert: *Compt. rend.*, **145,** 378 (1907). 45. Gaubert: *Compt. rend.*, **147,** 632 (1908). 46. Gaubert: *Compt. rend.*, **147,** 1483 (1908). 47. Gaubert: *Compt. rend.*, **49,** 1004 (1909). 48. Gaubert: *Bull. soc. min.*, **53,** 157 (1930). 49. Gaubert: *Revue gen. sci.*, **37,** 357 (1926). 50. Lehmann: *Ann. Phys.*, **51,** 47 (1894). 51. Gaubert: *Compt. rend.*, **194,** 109 (1932). 52. Gaubert: *Compt. rend.*, **155,** 649 (1912). 53. Ardagh, et al.: *Chem. and Ind.*, **53,** 1035 (1934). 54. Gaubert: *Compt. rend.*, **157,** 1531 (1913). 55. Neuhaus: *Chemie der Erde*, **5,** 529 (1930). 56. Kohlschütter and Egg:

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lize slowly by evaporation at room temperature. It is important to investigate both conditions of slow and of fast growth, since the habit-modifying effect of a cosolute may vary therewith.

The dye concentration was arbitrarily fixed at 0.03 g./100 cc. solution for NaF and NaCl, at 0.01 g./100 cc. for LiF, and at 0.01 g./10 cc. for KCl, KBr and KI. These amounts were frequently above the solubility of the dye. In many instances supplementary crystallizations were made at other dye concentrations; these are indicated in Table 2, summarizing the experimental data. No effort was made to estimate the minimum dye concentration necessary to effect habit variation, as was done in the work of Buckley.

Crystallizations made on a microscope slide are not very satisfactory, and this method was adopted only in lack of a practical alternative. There is a special tendency for the development of skeletonized or composite forms, some of which may simulate modified crystals. The instances of habit variation found in KCl, KBr and KI by this procedure, and described on following pages, were accepted only after repeated verification. It may also be noted that the small size of the crystals obtained on microscope slides usually precludes recognition of their color or pleochroism.

TABULATION OF EXPERIMENTAL RESULTS

The observed effect of dyes on the crystal habit of NaF, LiF, NaCl, KCl, KBr and KI is summarized in Table 2. The presence of the dye in the crystallizing solutions was also found in many instances to be accompanied by the development of pigmentation and anomalous pleochroism in the crystals, by super-saturation and rate-of-growth phenomena, and by the development of skeletal growths. These effects are described in following sections.

TABLE 2. TABULATION OF EXPERIMENTAL RESULTS WITH DYES

Dye concentration = 0.03 g./100 cc. solution for NaF and NaCl, 0.01 g./100 cc. for LiF, and 0.01 g. /10cc. for KCl, KBr and KI. Supplementary crystallizations at other dye concentrations are indicated in footnotes. The pure-solution habit of the halides listed is cubic.

Colour index number refers to the Colour Index: *Society of Dyers and Colourists*, Bradford, Yorkshire, **1924**, E. M. Rowe, editor.

Key to symbols: $a = \{100\}$; $o = \{111\}$.

Colour index	Dye	Acid NaF^4	LiF	NaCl	KCl	KBr	KI	Acid NaF^4
5	Napthol Green B	a^1	a	a	a	a		a
9	Martius Yellow	a						a
10	Napthol Yellow S	a^1	a	a	a^3			a
16	Fast Yellow G	a	a	a		a	a	a
21	Chrysoidine R	a		a	a	a	a	a
26	Croceine Orange	o^1	a	a^1	a^3	a^3	a^3	a
27	Orange G	a	a	a				a
29	Chromotrope 2R	a			a^3	a	a	a
30	Acid Fuchsine	a				a^3	o	a
31	Pontacyl Carmine 2G	a	a	a	a	a	a	a
40	Pontachrome Yellow 3RN	a		a	a			
56	Chromotrope 6B	a				a	a	a
57	Pontacyl Carmine 6B	a	a			a		a
63	Orange GT	a						a
77	Palatine Scarlet	a^2	a	a	a			a
79	Xylidine Red	a^2	a	a				a
80	Ponceau 3R	a	a					
88	Bordeaux B	a						a
89	Crystal Ponceau	a	a	a				a
98	Chrome Brown R	a						
99	Chrome F	a						a
138	Metanil Yellow	a	a	a	a			a
142	Orange III	a	a	a	a			
143	Orange IV	a	a	a				
144	Brilliant Yellow S	a	a	a	a^3	a	o	
148	Resorcin Yellow	a	a	a	a			a
150	Orange I	a	a	a	a			
151	Orange II	a						
161	Orange RO	a						
170	Solochrome Black	o^2		a^1		a		a
176	Fast Red A	a^1		a	a			a
179	Azorubin	a	a	a	a			
180	Fast Red VR	a		a	a			
181	Azo Red A	a						
182	Aceko Fast Red	a						
183	Newport Croceine Scarlet	a						
184	Amaranth	a						

TABLE 2. TABULATION OF EXPERIMENTAL RESULTS WITH DYES—*Continued*

Colour index	Dye	Acid NaF[4]	LiF	NaCl	KCl	KBr	KI	Acid NaF[4]
185	Brilliant Scarlet	a^2		*a*	*a*			
186	Ponceau 6R	*a*	*a*	*a*				
188	Chromotrope 8B	*a*						
197	Superchrome Yellow RN	*a*		a^3	o^3	a^3	a^3	
203	Pontachrome Black K	*a*						
204	Solochrome Black A	*a*						
252	Croceine Scarlet N ex.	*a*						
277	Croceine Scarlet 3B	a^1	*a*	*a*	*a*			
280	Biebrich Scarlet	*a*						
286	Croceine Scarlet 7B	*a*	*a*	*a*	*a*			
310	Napthyl Blue-Black N	*a*		*a*	*a*			
311	Naphthol Black 6B	*a*		*a*	*o*			*a*
313	Brilliant Croceine 9B	a^2	*a*	a^2	o^3	o^3	*a*	*a*
314	Diamine Blue 6G	*a*	*a*	*a*	*a*			
315	Napthol Black 3B	a^1	*a*	*a*	*a*	*a*		
316	Diaminogen Blue NA	*a*		*a*	*a*			
353	Pontamine Fast Pink BL	a^2	*a*	a^1	*a*			
370	Congo Red	*a*	*a*					
406	Pontamine Blue BBF	*a*		*a*	o^3			
443	Acid Anthracene	*a*	*a*					*a*
448	Benzopurpurin 4B	*a*	*a*					
449	Benzopurpurin 6B	*a*						
463	Azo Blue	a^2	*a*	*a*				
471	Dianil Azarine	a^1		a^1				
472	Diamine Blue BX	a^2	*a*	a^1	*a*			
473	Columbia Blue G	a^1		*a*	*a*	*a*		
474	Chicago Blue R	*a*		*a*	*a*			
477	Newport Direct Blue 3B	a^2	*a*	*a*	*a*			
480	Chrysamine R	*a*						
475	Eboli Blue 6A	*a*		*a*	*a*			*a*
512	Chicago Blue RW	*a*		*a*	*a*		*a*	*a*
520	Diamine Sky Blue A	a^1						
582	Direct Deep Black E ex.	*a*		*a*	*a*			
621	Direct Orange G	*a*			*a*			
622	Pontamine Yellow XSG	*a*		*a*	o^3			
624	Diphenyl Citronine G	*a*			*a*			
640	Tartrazine	*a*	*a*	*a*				
655	Auramine	—	*a*					
657	Malachite Green	—						
670	Light Green SF yellowish	a^1						
677	Basic Fuchsin	*a*						
680	Methyl Violet	*a*			*a*			
680	Gentian Violet	*a*						
681	Crystal Violet	a^1						
692	Acid Magenta	—						

TABLE 2. TABULATION OF EXPERIMENTAL RESULTS WITH DYES—*Continued*

Colour index	Dye	Acid NaF[4]	LiF	NaCl	KCl	KBr	KI	Acid NaF[4]
695	Acid Violet 4BN	*a*	*a*	*a*	*a*			
698	Formyl Violet S4B	*a*	*a*	*a*	*a*	*a*	*a*	
703	Methyl Alkali Blue	a^1						
707	Soluble Blue	*a*						
712	Patent Blue	a^1				*a*	*a*	
715	Cyanol Extra	a^1	*a*	a^1	a^3	*a*	*a*	
749	Rhodamine B	*a*		*a*	*a*			
766	Uranine	*a*						
766	Fluoresceine	*a*		a^2	*a*			
768	Eosine	a^1						
773	Erythrosine	a^1		*a*	*a*			
774	Phloxine	*a*		*a*	*a*			
777	Rose Bengale	*a*		*a*	*a*			
779	Rose Bengale 3B	*a*		*a*	*a*			
801	Quinoline Yellow	*a*	*a*	*a*	*a*			
841	Safranine A	a^1		*a*	*a*			
842	Methylene Violet 2RA	*a*	*a*	*a*	*a*	*a*	*a*	
861	Induline Soluble	*a*						*a*
865	Nigrosine WSB	*a*						
922	Methylene Blue	a^1						
1027	Alizarin NAC 20%	*a*						
1081	Anthraquinone Green GX	a^2	*a*	*a*	*a*			
1034	Alizarin Red S	o^2		a^1	a^3	*a*	*a*	*a*, *o*
1085	Alizarin Blue Black B	a^1		*a*	o^3			
1087	Alizarin Cyanol EF	*a*						
1089	Anthraquinone Blue SR	a^2		a^1				
1180	Acid Blue GR conc.	*a*						
1238	Turmeric	a^1						
1239	Cochineal	*a*						
1246	Haematoxylin	o^2						

[1] Also at 0.1 and 0.01 g. dye/100 cc. solution.

[2] Also at 0.1, 0.01 and 0.001 g. dye/100 cc. solution.

[3] Also at 0.05 and 0.001 g. dye/100 cc. solution.

[4] Solution containing 1 cc. 6N HCl per 100 cc.

DESCRIPTION OF HABIT VARIATION AND OPTICAL EFFECTS

Effect of Dyes on NaF

Habit Variation. Four of the 112 dyes tried with NaF effected variation in habit from cubic to octahedral. The effective dyes were Croceine Orange, Solochrome Black, Alizarin Red S, and Haematoxylin. Only a crude Haematoxylin preparation was available, and parallel results were not obtained in check crystallizations. The octahedra obtained with this substance and with Alizarin Red S were deep red to red-brown in color.

The presence of free alkali has been found (3) to increase the habit-varying property of dyes containing carboxyl groups and to decrease the effectiveness of sulphonate dyes containing hydroxyl groups. No experiments in this direction were made with NaF since free hydroxyl itself is markedly effective in changing the habit of NaF. The addition of free acid (HCl) to the solutions was found to be without action on many of the non-effective dyes (Table 2), although it markedly favored the formation of normal cubes in place of the skeletal cubes, described beyond, commonly obtained with NaF from solutions containing dyes. The effective dyes, Croceine Orange and Solochrome Black, however, lost their effectiveness in acid solutions. Alizarin Red S remained effective in faintly acid solutions.

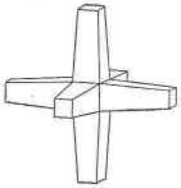

Fig. 1

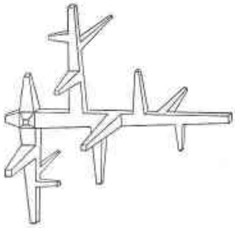

Fig. 2

Skeletal Growths. Skeletonized cubes of NaF were obtained quite generally from solutions containing the ineffective dyes. A few dyes, notably Anthraquinone Green GX, were without a marked skeletonizing effect. This is a special effect associated with the presence of dye, since NaF crystallizes from pure water solutions as ordinary cubes. Moreover, the effect is found only with NaF and LiF and is almost always lacking with the alkali chlorides, bromides and iodides. The skeletal growths typically consist of six tapering arms at 90° to each other and bounded laterally and at the terminations by $\{100\}$ faces (Figs. 1 and 2). The degree of complexity of the growths varies from cubical forms with short stubby arms extending from one or more faces to complex, rectangular, lattice-like growths with hundreds of subsidiary branching arms. The growths usually range in size from 1 to 3 mm., but occasionally extend up to 10 mm. or more. Most crystallizations afford the simple type of Fig. 1 mixed with a small proportion of ordinary cubes and more complex growths.

The action of different dyes in promoting skeletal growths varies widely. In particular, Fast Red A, Diaminogen Blue NA, Pontamine Fast Pink BL, Direct Deep Black E, Pontamine Yellow XS and Cochineal caused the development of extraordinarily complex and delicate lattice-like growths, together with needle-like single-crystal cubes a centimeter or more in length. These growths formed in the solution as dense bulbous aggregates of a pasty consistency. Similar effects can be obtained with other dyes at relatively high concentrations. Buckley has also noted (4) that remarkably delicate skeletal growths are produced in $KClO_3$ by Congo Red, Benzopurpurin 4B and other colloidal dyes.

The skeletonizing effect of the dyes is lost if the solutions are made acid. Under such conditions ordinary cubes are obtained, which, however, may be tinted or pleochroic as from non-acid solutions. Skeletonized cubes of NaF are also obtained from solutions containing hydroxyl-affording inorganic cosolutes.

Crystallization-Interference Effects. Many dyes were found to cause super-saturation in solutions of NaF and the other alkali halides. In general, the effect was most marked in NaF with dyes that possessed a special skeletonizing influence, or that caused habit variation. It was also remarked that dyes which effected habit variation in one halide and not in others had a relatively marked influence on the super-saturation of the unmodified halides.

Similar observations have been made by Wenk (5) and by Marc and and Wenk (6), who found that marked super-saturation was induced in K_2SO_4 and other substances by dyes which strongly colored the crystals or which modified their habit. Yamamoto (7) found that the particular cosolutes which increased the size of KCl and NH_4Cl crystals produced super-saturation in solutions of those substances.

The super-saturation in these instances is a result of the adsorption of the dye or cosolute on the nuclei tending to form in the solution, peptizing them and, in a sense, forcing them back into solution. When nuclei are finally forced through the threshold size barrier by increasing super-saturation, the adsorption may be expressed by a pigmentation of the crystals, by habit variation, or by an increase in the average size of the crystals as a consequence of the fewer number of nuclei present in the solution. The adsorption may also, by slowing the over-all rate of growth of the crystals, increase their perfection and transparency.

Coloration. Many dyes were found to afford deeply colored cubes or skeletal cubes of NaF. These dyes are listed in Table 3. A number of instances of faint coloration were excluded from this list. The occurrences are significant in that they identify {100} as the selectively adsorbing plane. No habit variation accompanies such adsorption since {100} is the ordinary habit of NaF.

TABLE 3. DYES ADSORBED BY {100} OF NaF

Croceine Orange
Pontachrome Yellow 3RN
Chromotrope 6B
Bordeaux B
Chrome F
Pontachrome Black K
Solochrome Black A
Resorcin Yellow
Napthyl Blue Black N
Napthol Black 6B
Brilliant Croceine 9B
Diamine Blue 6G
Napthol Black 3B
Diaminogen Blue NA
Pontachrome Fast Pink BL
Pontachrome Blue BBF
Acid Anthracene
Dianil Azarine
Diamine Blue BX
Columbia Blue G
Chicago Blue R
Eboli Blue 6A
Newport Direct Blue
Chicago Blue RW
Direct Deep Black E extra
Direct Orange G
Pontamine Yellow XSG
Diphenyl Citronine G
Acid Violet 4BN
Formyl Violet S4B
Methyl Alkali Blue
Rose Bengale
Induline Soluble
Nigrosine WSB
Anthraquinone Green GX
Alizarin Blue Black B
Anthraquinone Blue SR
Acid Blue GR conc.

Pigmentation of the crystals due to a mechanical enclosure of dye crystals or particles, or to the presence of negative crystal cavities containing dye solution was not observed.

Anomalous Pleochroism. Examination in polarized light of the dye-tinted crystals described above revealed numerous instances of anomalous pleochroism. A list of the dyes affording this effect, together with a statement of the optic orientation, is given in Table 4. The occurrence of anomalous pleochroism in dye-tinted crystals was first described by de Senarmont, in 1854, and was later studied in detail by Gaubert (8) and Buckley (25). The pleochroism arises from the oriented enclosure of dye molecules or of dye crystals, which impress their own optical behavior on the host crystal. Anomalous pleochroism is also found in natural crystals that contain a foreign pigmenting substance. The natural crystals of NaF (*villiaumite*) are deep carmine in color and pleochroic, but these effects are due to radioactivity.[a]

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[a] Villiaumite occurs in nepheline syenite pegmatite as anhedral masses with marked dichroism in carmine red (*o*) and gold (*e*). The crystals are anomalously weakly birefringent, with extinction parallel to rows of negative crystal cavities or inclusions (arranged parallel {100}?). *X*-ray examination proves the crystals to be identical with artificial NaF (Barth, T., and Lunde: *Centr. Min.*, 57, **1927 A**).

TABLE 4. DYES PLEOCHROIC IN NaF

Dye	Relation of [100] to vibration direction	
	Parallel	Perpendicular
Croceine Orange*	yellow	golden-yellow
Bordeaux B*	yellow-rose	rose
Diamine Blue 6G	lavender	blue
Napthol Black 3B	violet	light violet
Pontamine Fast Pink BL	yellow	red-orange
Dianil Azarine	lavender	blue
Diamine Blue BX	lavender	blue
Columbia Blue G	lavender	blue
Eboli Blue 6A*	light purple	purple
Induline Soluble*	light purple	purple
Anthraquinone Green GX	light green	dark green
Anthraquinone Blue SR	light blue	blue

* In solutions made faintly acid with HCl.

EFFECT OF DYES ON LiF

None of the 39 dyes investigated with LiF effected variation from the ordinary {100} habit of this substance. With but few exceptions skeletal cubes, similar to Figs. 1 and 2 admixed with normal cubes, were obtained from the dye crystallizations. A few dyes, among which may be mentioned Orange I, Solochrome Black, and Croceine Orange, interfered markedly with the crystallization and tended to produce extraordinarily delicate lattice-like growths and needle crystals. The latter two dyes effected habit variation in NaF.

Coloration. Anomalous Pleochroism and Birefringence. Anomalous pleochroism was noted only with Diamine Blue BX. A number of other dyes were adsorbed by {100}, and afforded tinted cubes and skeletal cubes, but without pleochroism. These dyes are listed in Table 5. Coloration and pleochroism were difficult to recognize with LiF because of the small size of the crystals formed by this substance. Several dyes, notably Newport Direct Blue, Solochrome Black, Diamine Blue 6G, and Napthol Black 3B, when present in relatively high concentrations caused the formation of minute, deeply tinted, irregular granules of LiF.

TABLE 5. DYES ADSORBED BY {100} OF LiF

Napthol Yellow S
Palatine Scarlet
Orange III
Resorcin Yellow
Solochrome Black
Croceine Scarlet 3B
Diamine Blue 6G
Napthol Black 3B
Congo Red
Diamine Blue BX
Acid Anthracene
Benzopurpurin 4B
Azo Blue
Newport Direct Blue 3B
Acid Violet 4BN
Formyl Violet S4B
Anthraquinone Green GX

Strong anomalous birefringence was found to be produced in LiF by the colloidal dyes Congo Red and Benzopurpurin 4B. The dyes tinted the crystals deep red. The birefringence was developed in the growth sectors beneath the {100} faces, with extinction parallel to the cube edges.

Effect of Dyes on NaCl

None of the 62 dyes investigated with this substance was found to effect habit variation from the ordinary cubical habit. A number of dyes, however, interfered with the crystallization. Here may be mentioned Chromotrope 2R, Acid Fuchsin, Fast Yellow G, Brilliant Croceine 9B and Methylene Violet 2RA. Several of these dyes effected variation in habit with other halides.

The skeletal growths produced in NaF and LiF by dyes were not observed with NaCl. Hopper-shaped crystals, however, often formed at the surface of the evaporating solution.

The cubes of NaCl obtained in the crystallizations quite generally were opaque and possessed little mechanical strength. These characters appeared to be due to the existence of minute elongated cavities in the crystals disposed parallel to the cube edges, probably resulting from a tendency for hopper-growth. For this reason the possibility could not be excluded that the color of the crystals was due to the mechanical enclosure of dye-tinted mother liquid.

Effect of Dyes on KCl

The crystallizations of this substance were made on a microscope slide, as previously described. Five of the 56 dyes investigated were found to produce a variation to octahedral from the ordinary cubical habit. These dyes were Brilliant Croceine 9B, Superchrome Yellow RN, Napthol Black 6B, Pontamine Blue BBF and Pontamine Yellow XSG. A doubtful effect was noted with Chromotrope 2R and Alizarin Blue Black B, and it is possible that other instances went unrecognized.[a]

The super-saturation effects noted with NaF, LiF and NaCl were relatively marked with KCl, KBr and KI. Brilliant Yellow S, Chrome 2R and the habit-varying dyes previously named were quite effective in this

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[a] In observing crystallizations of alkali halides extreme care should be taken to distinguish between true modifying faces and attachment faces. The latter are single faces developed on the cubes that form at the surface of the solution, and represent the surface by which the crystals hung at the liquid interface. The face invariably approximates in position to {111} and often is perfectly plane and lustrous. Such attachment faces on NaCl and other halides were erroneously described by Retgers, J. W. (*Zeits. anorg. Chem.*, **9**, 267, 1892) as true modifying faces, under the name "one-corner modification." When such crystals sink and rest upon the slide they closely simulate octahedra or cubo-octahedra when viewed directly from above.

respect with KCl. The effect, however, appeared to be produced by any soluble dye if present in sufficiently large concentration. Marked supersaturation was observed even in cold KCl solutions.

Rate of Growth Effects. The effectiveness of the dyes in producing change in habit varied with the rate of growth of the KCl crystals. Only cubes were formed during the first stages of cooling of the dye-containing solution. Under these conditions the crystals grow rapidly, as a consequence of the marked temperature rate of change of solubility. As the solution cools and the crystals grow more slowly, octahedral faces appear on the cubes. Finally, under conditions of very slow growth by evaporation at room temperature, complete octahedra are formed. The effect of rapid growth in counter-acting the habit-varying influence of a cosolute was early recognized by Beudant (1818) and by Necker (1837), and many additional instances are to be found in more recent literature. The variation in habit with rate of growth of crystals formed from pure solution was first remarked in 1669 by Robert Boyle, who also noted the effect of impurities in causing habit variation.

Effect of Dyes on KBr

No well-defined instances of habit variation were found among the 20 dyes investigated. Brilliant Croceine 9B interfered with the crystallization and in one experiment afforded irregular cubical crystals with small unequally developed {111} faces. Efforts to verify this observation were unsuccessful.

Effect of Dyes on KI

Of the 16 dyes investigated only Acid Fuchsin and Brilliant Yellow S effected variation in habit. Both dyes caused the development of cubo-octahedra and octahedra under conditions of slow growth. These dyes were also found to interfere with the crystallization of other of the halides, but without changing the habit.

DISCUSSION

Dye Adsorption Theory of Buckley

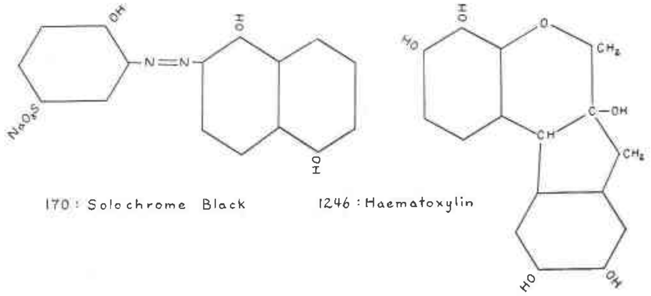
Buckley has concluded (3, 4) that the mode of attachment of dyes and of foreign inorganic ions of the RO_x-type to growing crystals of oxysalts is identical in nature. The seat of the attaching power in the dye molecule is located in the substituent SO_3Na groups. The oxygen-triangles in these groups appear to substitute for oxygen-triangles of similar size and shape in the oxysalt, in the same manner that tetrahedral inorganic anions of the RO_x-type substitute for $SO_4^=$ in K_2SO_4 crystals.

The substitution, or adsorption, of the polar groups in this way serves to anchor the rest of the dye nucleus, which is inert in itself, to the adsorbing surface. Because of the great bulk of the dye molecule, the habit-varying effect may be 50 to 100 times that of an inorganic ion. Other factors which have been found to influence the adsorption include the number of the substituent polar groups and their position on the dye nucleus, the composition of the group itself, and the *pH* of the solution.

It is not possible to explain the adsorption of dyes by crystals of the NaCl-type alkali halides on this basis. An attachment of dye by the substitution of sulphonate groups into the halide structure is not feasible, for structural reasons. The halide anions differ in charge and, with the exception of F^-, in size from the oxygen atoms of the sulphonate groups. Further, anion configurations compatible in shape and dimensions with the oxygen-triangles of the SO_3Na groups do not exist in the halides. While a triangular configuration is found in (111) of the halides, the inter-ionic distances are too great to permit a substitutional meshing by the oxygen-triangles of the dyes. In (111) planes the triangle-side for LiF is 2.84 Å, for NaF 3.26 and the values increase in the series $Li^+ \rightarrow Rb^+$ and $F^- \rightarrow I^-$ to 4.98 in KI and 5.18 in RbI. These values compare with a probable value of 2.6 Å or less for the oxygen-triangles of the SO_3Na groups.

The adsorption of dyes by precipitated AgCl (a NaCl-type substance) is viewed by Kolthoff (9) as an exchange adsorption between the dye ions and crystal ions of the same sign immediately adjacent to the surface of the AgCl crystal. On the other hand, Verwey (10) views dye adsorption by precipitated AgCl as involving an exchange between the dye ions and counter-ions in the outer, diffuse, part of the double-layer enveloping the AgCl crystals. Neither mechanism appears adequate to account for the habit variation in the alkali halides. While the adsorption of dye in either of these two ways would slow the normal growth velocity of the adsorbing surface, and thus satisfy the essential condition for habit variation, there is no reason to suppose that the dye should be adsorbed on crystal faces other than those of the normal {100} habit. A mechanism of the type described by Verwey, in which the dye is loosely held adjacent to the crystal surface, seems very improbable in the present instance. The occurrence of coloration and, in particular, of anomalous pleochroism in the halide crystals indicates that the dye has in some way been directly attached to the crystal surface.

It is interesting to note that two hydroxyl-containing dyes, Solochrome Black and Haematoxylin (Fig. 3), effect habit variation to octahedral in NaF. Possibly the effect of these dyes is due to the substitutional attachment of the OH groups for F ions in the NaF, analogous to the substitution of SO_3Na groups into oxysalts. It may also be noted that sodium citrate is extremely effective in producing variation to octahedral in NaF. The citrate anion itself possesses substituent OH groups, to which the adsorption may be owing.



170 : Solochrome Black 1246 : Haematoxylin

FIG. 3

The other effective dyes do not appear to possess any common character, either in size, structure or in the kind and relative position of their polar groups, and the source of their habit-varying power is obscure.

DYE ADSORPTION THEORY OF FRANCE

France and co-workers have developed the idea that "if any given substance is going to adsorb a foreign substance the adsorption will take place at those faces having the strongest fields of force" (11). It is also held that crystals growing from pure solution should develop faces that have the least field of force. A test may be made of this theory using the same criterion accepted by France for the identification of supposed high field forms, namely, a geometrical distinction between planes populated solely by ions of the same sign (high field planes) and planes populated by both positive and negative ions (low field planes).

In substances of the NaCl structural-type the theory requires (111) to be the most strongly adsorbing form, and (100) and (110) to be weakly or non-adsorbing.[a] Survey of the instances of dye adsorption by crystals of this type shows, however, that adsorption by (111) is the exception and not the rule. Thus of the 59 instances of dye adsorption by NaF and LiF, as evidenced by habit variation, pleochroism or coloration, 55 are of adsorption by (100) planes and only 4 by (111) planes. A similar behavior is found with AgCl. Reinders (12) found that of 38 dyes, 15 were not taken up by the AgCl crystals, 5 produced dendritic growths of unknown habit, and 18 were taken up but without change from the normal (cubo-octahedral) habit. Gaubert, moreover, states from his own observations

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[a] In this structure-type all planes with h, k and l odd contain solely ions of the same sign.

(13) with AgCl and AgBr that the dye is selectively adsorbed by the {100} faces.

Numerous instances of the adsorption of inorganic cosolutes by the supposedly low field planes are also known. A list of such instances is given in Table 6. Doubtlessly most instances of the adsorption of colorless cosolutes by (100) in the alkali halides go unnoticed, since such adsorption is not made apparent by habit variation and must be shown by special methods.

TABLE 6. SELECTIVE ADSORPTION BY "NEUTRAL PLANES" IN NaCl-TYPE SUBSTANCES

Crystallized Substance	Cosolute	Adsorption Habit	Authority
NaCl	$HgCl_2$	(110)	Gille and Spangenberg; Royer; Orloff
NaCl	$AlCl_3$	(110)+(100)+(111)	Gille and Spangenberg
NaCl	$SbCl_3$	(110)+(100)+(111)	Orloff
NaCl	Ba(SbO) tartrate	(110), (210), (211), (332), etc.	Traube; Orloff
NaCl	glycocoll	(210), (310), etc.	Orloff
NaCl	urine	(543)?	Knop
NaCl	Bi^{+3}	(110)	Yamamoto
NaCl	Cd^{+2}	(110)	Yamamoto
NaCl	Pb^{+2}	(100)	Gibbs and Clayton; Hahn; and others
NaCl	propionic acid	(210)+(100)+(111)	Groth
KCl	urea	(100)	France
KCl	urine	(411)	Knop
KCl	wormwood extract	(211)	Claasen
KCl	Bi^{+3}	(110), (210)	Yamamoto
KCl	Pb^{+2}	(100)	Hahn
KBr	$PbBr_2$	(110)	Retgers
KBr	urea	(100)	France
NaF	H_3BO_3	(110)	Frondel
RbCl	Ti^{+3}	(110)	Yamamoto
RbCl	ZrO^{+2}	(210)?, (111)	Yamamoto

Several objections of a more general nature to the theory of France may now be pointed out. The theory itself is based on the fundamental assumption that there are differences in surface energy between faces of crystals which are significant with regard to crystal growth and adsorption. This assumption, however, is subject to a restriction which denies the application of the theory to the growth and adsorptive behaviors of macroscopic crystals. As shown by Willard Gibbs (14), sub-microscopic crystals are in equilibrium with their solution when their bounding faces are those of minimum surface energy. This applies, however, only to crystals below about 0.001 mm. in size, i.e., to crystals in the size range where the surface area, which is the capacity factor of surface energy, is relatively greatly developed. With macroscopic crystals the differences in surface energy between different crystal faces are practically equal to zero and are without influence on the habit development (15). The restriction was realized by Gibbs but not by Curie (16), who later independently expressed a similar theory. The size above which surface energy differences between faces become negligible was estimated in this connection by Berthoud (17), from the relation between particle size and solubility found by Hulett (18).

Experimental verification of this qualification in point of size is found in the observed equilibrium behavior of crystal spheres and polyhedra in saturated solutions (19). Cottrell (20) also concluded from experiments on the behavior of NaCl octahedra in saturated NaCl solutions that the Gibbs relation did not hold for macroscopic crystals. The theory of France fails for this reason. Explanation of the adsorptive behavior of macro-crystals—which itself is largely at variance with the proposed relation, accepting the criteria for high field faces given by France—must be sought in some other direction.

The growth mechanism of macroscopic ionic crystals of the NaCl-type has been semi-quantitatively analyzed by Kossel (21) and by Stranski (22), from consideration of the energy changes accompanying the removal from solution, dehydration and ordered packing of ions into the structure. The general point of view of France cannot be reconciled with this work, in which growth and adsorption are related directly to the geometrical situation of the surface ions and the crystal chemistry of the substances involved, rather than to areal surface energies.

France also concludes (23) from an observed identity of cell dimensions of pure and of dye-tinted crystals that the dye is adsorbed interstitially. This conclusion is unjustified. The identification of a solid solution effect as substitutional, interstitial or omission, and the distinction of these from a purely mechanical enclosure of foreign materials, requires the application of criteria (24) beyond the measurement of cell dimensions. Further, variation in cell dimensions in itself is not a necessary concomitant of any type of solid solution.

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