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THE FORMATION OF TWO LIQUID PHASES IN INORGANIC SYSTEMS

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INTRODUCTION

The phenomenon of complete or partial mutual insolubility of inorganic substances in the liquid state (formation of separate layers) is encountered in various fields, such as metallurgy, glassmaking, geology, etc. Although the mechanism of separation into two or more phases has been clarified by the concept of the possible existence of microheterogeneous liquids[1], there is still no general theory of the solubility of one substance in another, nor any theory

explaining the phenomenon of partial miscibility[2-4]. The thermodynamics of binary systems, worked out by van Laar[5] and Mlodzeevskii[6] in terms of thermodynamic potential–composition diagrams, answer the question whether or not a given system will separate into two layers, but the calculation of specific thermodynamic potentials is very difficult owing to our ignorance of many thermodynamic constants. Furthermore, the thermodynamic potentials characterise only the state of a system, and give no information about the nature of immiscibility.

On this point, the view of van der Waals[7] may be regarded as generally accepted; according to this mutual insolubility in the liquid state results from a considerable difference between the intermolecular forces ("internal pressures") in the two phases. Two liquids which have similar internal pressures are miscible with one another in all proportions; when the difference in internal pressure is considerable, the liquids are completely or partly insoluble in one another. Since the internal pressure is closely linked to the macroscopic properties, such as coefficients of expansion and compressibility, surface tension, heats of vaporisation, etc., two immiscible liquids should differ markedly from one another in these macroscopic properties. The relation between phase separation and the surface tension of immiscible liquids was first demonstrated by Antonov[8], and later by other workers[9-11]. Semenchenko and Davydovskaya[2] showed experimentally, and explained in terms of the Boltzmann principle and the concept of "generalised moments", that addition of a third component which increases the surface tension of one of the liquids diminishes the mutual solubility, raising the upper and lowering the lower consolute temperatures.

The present survey attempts to systematise and generalise the considerable amount of experimental data on the formation of two liquid phases in inorganic systems (other than metallic systems); most of this has been published during the past 10–15 years.

More than 150 inorganic systems forming two liquid phases are now known and are divided into three types, AX–BY, AX–BX, and AX–AY, according to the nature of the components and the origin of the separation.

TABLE 1. AX–BY system which form two liquid phases.

	System	$\frac{P_{AX}}{P_{BY}}$	$\frac{\mu'_A}{\mu'_B}$	$\frac{\mu_A}{\mu_B}$	$\frac{\mu_X}{\mu_Y}$	Reference
1	$LiNO_3$ — AgCl			1.44	1.14	17
2	$NaNO_3$ — AgCl			1.15	1.41	17
3	KNO_3 — AgCl			0.84	1.41	18
4	$TlNO_3$ — AgCl			0.74	1.41	18
5	$Ca(NO_3)_2$ — AgCl					19
6	Li_2SO_4 — AgCl			1.44	0.81	
7	Na_2SO_4 — AgCl			1.15	0.81	18
8	Li_2WO_4 — AgCl			1.44	0.96	20
9	$LiVO_3$ — AgCl			1.44		21
10	$NaVO_3$ — AgCl			1.15		21
11	KVO_3 — AgCl			0.84		21
12	Na_2CrO_4 — AgCl			1.15		21
13	Na_2MoO_4 — AgCl			1.15		21
14	Na_2WO_4 — AgCl			1.15		21
15	$NaNO_3$ — AgBr			1.15	1.28	17
16	KNO_3 — AgBr			0.84	1.28	18
17	Li_2CrO_4 — AgBr			1.44		21
18	Li_2MoO_4 — AgBr			1.44		21
19	Li_2WO_4 — AgCl			1.44		21
20	$LiVO_3$ — AgCl			1.44		21
21	Li_2SO_4 — AgBr			1.44		21
22	Na_2CrO_4 — AgBr			1.15		21
23	Na_2MoO_4 — AgBr			1.15		21
24	Na_2WO_4 — AgBr			1.15		21
25	Na_2SO_4 — AgBr			1.15		21
26	$NaVO_3$ — AgBr			1.15		21
27	KVO_3 — AgBr			0.84		21
28	LiCl — AgI	1.26	1.82	1.44	1.22	22
29	NaCl — AgI	1.30	1.49	1.15	1.22	22
30	$NaNO_3$ — AgI			1.15	1.13	17
31	KNO_3 — AgI			0.84	1.13	23
32	$TlNO_3$ — AgI			0.76	1.13	24
33	KNO_3 — TlBr			1.12	1.28	25
34	Na_2SO_4 — TlBr			1.52	0.75	26
35	KNO_3 — TlI			1.12	1.13	18
36	Li_2SO_4 — $CdCl_2$			0.66	0.81	27
37	Li_2CrO_4 — $CdBr_2$			0.63		21
38	CsCl — LiF	0.99	2.16	2.10	1.36	28
39	CsBr — LiF	0.96	2.22	2.10	1.47	28
40	$PbCl_2$ — Ag_2S	1.76	1.04	0.59	0.48	29
41	Li_2SO_4 — $PbCl_2$			0.85	0.81	30
42	LiF — PbO	3.30	2.57	0.85	2.03	
43	NaF — PbO	3.34	2.06	0.68	2.03	21,31
44	KCl — PbO	3.20	1.45	0.50	2.79	21
45	NaCl — PbO	3.10	1.93	0.68	2.79	21
46	RbCl — PbO	3.22	1.32	0.44	2.79	21
47	NaBr — PbO	2.96	1.50	0.68	3.00	21
48	KF — PbO	3.40	1.26	0.50	2.03	21
49	KBr — PbO	3.10	1.41	0.50	3.00	21
50	KI — PbO	3.00	1.36	0.50	3.50	21
51	Li_2SO_4 — PbO			0.85	2.25	21
52	Na_2SO_4 — PbO			0.68	2.25	21
53	K_2SO_4 — PbO			0.50	2.25	21
54	Li_2WO_4 — PbO			0.68	2.69	21
55	Na_2WO_4 — PbO			0.68	2.69	21
56	K_2WO_4 — PbO			0.50	2.69	21
57	Na_2CrO_4 — PbO			0.68	2.25	21
58	Na_2MoO_4 — PbO			0.68	2.69	21
59	K_2MoO_4 — PbO			0.50	2.69	21
60	Na_2CrO_4 — PbO			0.68	2.25	21
61	Na_2MoO_4 — PbO			0.68	2.69	21
62	K_2MoO_4 — PbO			0.50	2.69	21
63	K_2CrO_4 — PbO			0.50	2.69	21
64	Li_2CO_3 — PbO			0.85	1.96	21
65	Na_2CO_3 — PbO			0.68	1.96	21
66	K_2CO_3 — PbO			0.50	1.96	21
67	Na_2TiO_3 — PbO			0.68		21
68	K_2TiO_3 — PbO			0.50		
69	NaCl — B_2O_3	1.63	9.00	0.07	2.79	
70	KCl — B_2O_3	1.67	11.9	0.05	2.79	
71	Na_2SO_4 — B_2O_3			0.07	2.25	
72	NaCl — TiO_2	2.30		0.16	2.79	
73	KCl — TiO_2	2.37		0.12	2.79	
74	CaS — SiO_2			0.19	1.33	32
75	FeS — SiO_2	0.30	1.33	0.30	1.33	32
76	MgF_2 — SiO_2			0.25	0.5	33,34
77	CaF_2 — SiO_2			0.18	0.5	33,34
78	SrF_2 — SiO_2			0.15	0.5	33,34
79	BaF_2 — SiO_2			0.14	0.5	33,34
80	KCl — $Na_2B_4O_7$*			0.7		35
81	NaCl — $K_2B_4O_7$			0.7		35
82	NaF — $PbTiO_3$*			0.68		31
83	$LiSO_4$ — V_2O_5					
84	$CaSO_4$ — $Na_2B_4O_7$*			0.5		36
85	Na_2MoO_4 — $PbTiO_3$*			0.68		
86	K_2MoO_4 — $PbTiO_3$*			0.50		37
87	Na_2CO_3 — $PbTiO_3$*			0.68		
88	K_2CO_3 — $PbTiO_3$*			0.50		
89	K_2CO_3 — $PbZrO_3$*			0.50		
90	Na_2CO_3 — $PbZrO_3$*			0.68		

I. AX–BY SYSTEMS

Diagonal Sections (Composition Squares) of Reciprocal Ternary Systems

Table 1 gives all known AX–BY systems which separate into two liquid phases. For some of them values are given for the relative polarities of the compounds AX and BY*, the relative generalised ionic moments** μ_A/μ_B and μ_X/μ_Y [12,13], and the relative generalised moments of the cations μ'_A/μ'_B corrected for the effective charges on the ions.

All AX–BY systems can be divided into two groups, according to the manner in which layers are formed. Group (*a*) comprises systems in which two layers are formed in consequence of the mutual insolubility of the components AX and BY in the liquid state. In these systems a solid phase (the more infusible component) is in equilibrium with two liquids consisting mainly of component AX and component BY respectively. Group (*b*) comprises systems in which the cause of separation is not the complete or partial mutual insolubility of the molten components, but the decomposition of one of the components, e.g. BY, on melting, one of the resulting products being immiscible with molten AX. In these systems the solid phase is in equilibrium with two liquids consisting mainly of AX and a decomposition product of BY respectively.

Systems Ia. Among the ninety systems in Table 1, eighty (without asterisks) are Ia systems. They represent stable pairs of compounds of the corresponding reciprocal ternary systems A, B || X, Y, consisting either of simple compounds of the type of halides, oxides, sulphides, etc. (and therefore not triangulating sections of more complex systems), or else of a pair of simple compounds (halides, oxides, sulphides, etc.) and a pair of complex salts (nitrates, carbonates, sulphates, etc., predominantly of the alkali metals), and are therefore triangulating sections of more complex four-component systems involving six compounds A, B, C || X, Y (Fig. 1).

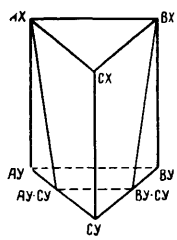


Fig. 1.

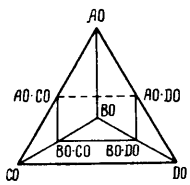


Fig. 2.

A survey of Ia systems, taking into account the characteristics of the components and the ions which they contain, allows several generalisations to be made about the conditions necessary for separation to occur.

From Table 1 the following conditions appear to be necessary for the formation of layers in AX–BY systems: one of the components must be a simple compound of comparatively low polarity* or a halide, an oxide, or a sulphide, etc. of a metal which yields a cation having an outer electron shell differing in structure from that of an inert gas (lead, thallium, silver, etc.), or even an acid anhydride B_2O_3, TiO_2, V_2O_5, etc; the other component is a typical salt, a halide, sulphate, nitrate, carbonate, etc., mainly of an alkali metal (only two systems are exceptions: LiF–CsCl and LiF–CsBr). Hence the compounds AX and BY should differ markedly from one another *in polarity*, and the two cations A and B must have electron shells of *different* structure, and differ markedly from one another in polarity [30] and generalised moments, and the corresponding atoms should differ in electronegativity. The anions X and Y should differ markedly from one another in their generalised moments, structure, valency, composition, and, if they are simple ions, in the electronegativity of their atoms.

These conditions do not contradict the effects noted earlier favouring the formation of layers [2,9–11,30].

Systems Ib. Only ten Ib systems are known (denoted by asterisks in Table 1). Three of these (Nos. 80–82) are diagonal sections of reciprocal ternary systems which are unstable sections of the prism formed by the six compounds A, B, C || X, Y (Fig. 1); the remaining systems are diagonal sections of reciprocal ternary systems which are unstable sections of tetrahedra representing the four oxides A, B, C, D || O (Fig. 2). One of the components of these systems, e.g. BY ($Na_2B_4O_7$, $PbTiO_3$, $PbZrO_3$) fuses with decomposition under the influence of the component AX. The decomposition product (B_2O_3, PbO) is not miscible with the component AX in the liquid state. This is readily seen from a more detailed examination of the systems Na, Pb || F, TiO_3 [31], Na, K || Cl, B_4O_7 [35], and Na, Ca || SO_4, B_4O_7 [36], which are sections of the corresponding prisms Na, Pb, Ti || O, F and Na, K, B || O, Cl (Figs. 3*a* and 3*b*) and the tetrahedron Na, Ca, B, S || O.

In the first system a small region of two liquid phases can be observed in the NaF–$PbTiO_3$ section adjacent to the NaF component. Separation occurring in the NaF–PbO lateral system (stable diagonal of the Na, Pb || F, O face of the prism in Fig. 3*a*), extending inside the prism in the plane of the NaF–PbO–TiO_2 triangle, covers only part of the NaF–$PbTiO_3$ section (Fig. 4) [31], which indicates that the Na, Pb || F, TiO_3 section of the Na, Pb, Ti || F, O prism is unstable in the liquid state. One of the two liquid phases in equilibrium with the solid phase consists mainly of sodium fluoride, and the other predominantly of lead oxide formed by the decomposition of lead titanate, which forms the solid phase. This means that lead titanate decomposes at a lower temperature (900°–950°) in molten sodium fluoride than in the pure state (1124°) [38].

In the Na, K || Cl, B_4O_7 system neither of the diagonal sections NaCl–$K_2B_4O_7$ and KCl–$Na_2B_4O_7$ can be stable, since other portions of the system, in this case the sides of the NaCl–$Na_2B_4O_7$ and KCl–$K_2B_4O_7$ composition squares,

* The poliarities P_{AX} and P_{BY} were calculated by Nekrasov's method [14, 15], and their values have been published [16].

** According to Semenchenko, the generalised moment of an ion is calculated by dividing its valency by its radius: $\mu = Z/r$.

The corrected generalised moment of a cation is calculated by dividing its effective charge by its radius: $u' = e/r$.

* The term "low polarity" is used in the sense of a considerable deviation from a purely ionic bond.

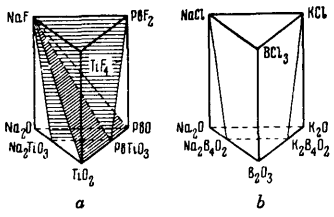


Fig. 3.

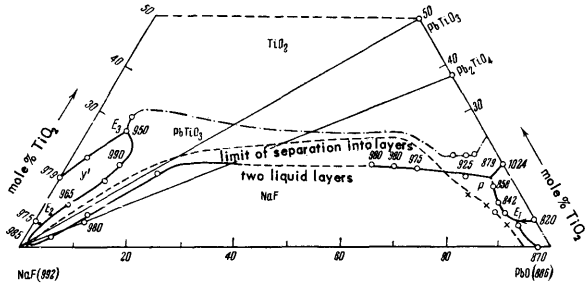


Fig. 4.

In the $Na_2B_4O_7-CaSO_4$ system [36], as in the preceding case, separation into layers is a consequence of the mutual insolubility of sodium and calcium sulphates in the boric anhydride formed by the decomposition of sodium and calcium tetraborates.

In the $Na_2CO_3-PbTiO_3$, $K_2CO_3-PbTiO_3$, $K_2MoO_4-PbTiO_3$, $NaCO_3-PbZrO_3$, and $K_2CO_3-PbZrO_3$ systems, which form parts of the corresponding tetrahedra Na(K), Pb, Ti(Zr), Mo(C) || O, separation into layers is due to decomposition of lead titanate or zirconate into lead oxide and the corresponding dioxide; lead oxide, sodium and potassium carbonates, and potassium molybdate are almost completely insoluble in one another. A diagram of the $K_2CO_3-PbTiO_3$ system shows clearly (Fig. 6) that separation into layers arising at the K_2CO_3-PbO side extends inside the triangle, covering the $K_2CO_3-PbTiO_3$ section. In this system, as in the $NaF-PbTiO_3$ one, lead titanate decomposes under the influence of potassium carbonate at 850°–900°, which is lower than with the pure compound.

It is clear from this brief survey of AX–BY systems that immiscible liquid phases are formed, independently of the complexity of the components, when one component is a simple compound of low polarity, typified by the halides, oxides, sulphides, etc. of metals whose cations do not have an inert gas structure (lead, silver, cadmium, thallium, etc.), or an acid anhydride (B_2O_3, V_2O_5, TiO_2). If neither of the components AX and BY is a compound of the above type, separation occurs only when such a compound is formed by decomposition of one of the components.

are unstable sections of other, more complex systems (in this case the faces of the prism, Fig. 3*b*), and hence the Na, K || Cl, B_4O_7 system itself is an unstable section of the prism in Fig. 3*b*, as is clear from the known principles relating to stable portions of complex systems [26]. That the $NaCl-Na_2B_4O_7$ and $KCl-K_2B_4O_7$ are unstable sections of the corresponding reciprocal ternary systems Na, B || Cl, O and K, B || Cl, O (faces of the prism in Fig. 3*b*) can be judged firstly from the data of Harrison [66], who showed cryoscopically that sodium tetraborate in molten sodium chloride is partly dissociated according to the equation

$$Na_2B_4O_7 = 2Na^+ + O^{2-} + 2B_2O_3;$$

and secondly by comparing the miscibility of sodium and potassium borates with that of boric anhydride in molten sodium and potassium chlorides respectively. The solubility of sodium and potassium chlorides in boric anhydride is considerably less than in the corresponding tetraborates [37], which is well shown for the sodium systems in Fig. 5, where data for part of the $NaCl-Na_2B_4O_7-B_2O_3$ ternary system are given. It is clear that $NaCl-B_2O_3$ forms a stable section of the reciprocal system, whereas the $NaCl-Na_2B_4O_7$ section is of subordinate importance, like, for example, the sections $4AgI.KI-KNO_3$, $KNO_3.KI-AgI$, or $AgNO_3.AgI-KNO_3$ and $2AgNO_3.AgI-KNO_3$ in the K, Ag || I, NO_3 system studied by Dombrovskaya and Koloskova [23]. Hence separation in $NaCl-Na_2B_4O_7$ and $KCl-K_2B_4O_7$ is a result not of immiscibility of the components but of a more complex interaction.

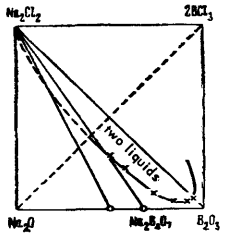


Fig. 5.

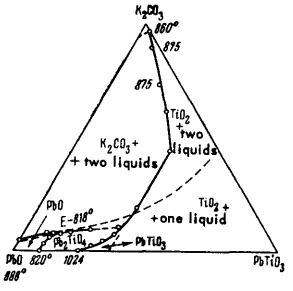


Fig. 6.

II. AX–BX SYSTEMS

All the AX–BX systems known to form immiscible liquid phases are listed in Table 2.

In these AX–BX systems one of the compounds (BX) is of low polarity and formed by a cation bearing three or four charges (B = Al, Si, B, Sb), while the other compound is a typical salt or basic oxide of a uni- or bivalent metal. Only in the $SbCl_3-SnCl_4$ system are both components of low polarity and non-saltlike. In all the systems the relative characteristics of the A and B ions favour separation into

TABLE 2. AX—BY systems which form two liquid phases.

No.	System	Compounds formed in systems	Solid phase in equilibrium with the two liquids	Reference
1	$NaBr - AlBr_3$	$NaBr \cdot AlBr_3$; $NaBr \cdot 2AlBr_3$ $2NaBr \cdot 7AlBr_3$; $x\ NaBr \cdot y\ AlBr_3$	$x\ NaBr \cdot y\ AlBr_3$	39
2	$KBr - AlBr_3$	$KBr \cdot AlBr_3$; $KBr \cdot 2\ AlBr_3$ $x\ KBr \cdot y\ AlBr_3$	$x\ KBr \cdot y\ AlBr_3$	40
3	$NH_4Br - AlBr_3$	$NH_4Br \cdot AlBr_3$; $NH_4Br \cdot 2\ AlBr_3$ $NH_4Br \cdot 3\ AlBr_3$; $x\ NH_4Br \cdot y\ AlBr_3$	$x\ NH_4Br \cdot y\ AlBr_3$	40
4	$AgBr - AlBr_3$	$AgBr \cdot AlBr_3$; $AgBr \cdot 2\ AlBr_3$	$AgBr \cdot 2AlBr_3$	40
5	$CaBr_2 - AlBr_3$	$CaBr_2 \cdot AlBr_3$; $x\ CaBr_2 \cdot y\ AlBr_3$	$x\ CaBr_2 \cdot y\ AlBr_3$	39,41
6	$BaBr_2 - AlBr_3$	$BaBr_2 \cdot 2\ AlBr_3$	$BaBr_2 \cdot 2\ AlBr_3$	40
7	$Hg_2Br_2 - AlBr_3$	$Hg_2Br_2 \cdot 2\ AlBr_3$	$Hg_2Br_2 \cdot 2\ AlBr_3$	40
8	$TlBr - AlBr_3$	$TlBr \cdot AlBr_3$; $TlBr \cdot 2\ AlBr_3$ $x\ TlBr \cdot y\ AlBr_3$	$x\ TlBr \cdot y\ AlBr_3$	40
9	$SnBr_2 - AlBr_3$	$SnBr_2 \cdot AlBr_3$; $SnBr_2 \cdot 2\ AlBr_3$;	$SnBr_2 \cdot 2\ AlBr_3$	40
10	$PbBr_2 - AlBr_3$	$PbBr_2 \cdot 2\ AlBr_3$	$PbBr_2 \cdot 2\ AlBr_3$	40
11	$NaCl - AlCl_3$	$NaCl \cdot AlCl_3$; $x\ NaCl \cdot y\ AlCl_3$	$x\ NaCl \cdot y\ AlCl_3$	40
12	$KCl - AlCl_3$	$KCl \cdot AlCl_3$; $x\ KCl \cdot y\ AlCl_3$	$x\ KCl \cdot y\ AlCl_3$	40
13	$NH_4Cl - AlCl_3$	$NH_4Cl \cdot AlCl_3$; $x\ NH_4Cl \cdot y\ AlCl_3$	$x\ NH_4Cl \cdot y\ AlCl_3$	40
14	$AgCl - AlCl_3$	$AgCl \cdot AlCl_3$; $x\ AgCl \cdot y\ AlCl_3$	$x\ AgCl \cdot y\ AlCl_3$	40
15	$BaCl_2 - AlCl_3$	$BaCl_2 \cdot 2AlCl_3$	$BaCl_2 \cdot 2\ AlCl_3$	40
16	$TlCl - AlCl_3$	$TlCl \cdot AlCl_3$; $TlCl \cdot 2\ AlCl_3$ $x\ TlCl \cdot y\ AlCl_3$	$x\ TlCl \cdot y\ AlCl_3$	40
17	$SnCl_2 - AlCl_3$	$SnCl_2 \cdot AlCl_3$; $SnCl_2 \cdot 2AlCl_3$ $x SnCl_2 \cdot y AlCl_3$	$x\ SnCl_2 \cdot y\ AlCl_3$	40
18	$SnCl_2 - SbCl_3$	$x SnCl_2 \cdot y SbCl_3$	$x\ SnCl_2 \cdot y\ SbCl_3$	40
19	$SbCl_3 - SnCl_4$	—	$SbCl_3$	40
20	$SrO - SiO_2$	$2SrO \cdot SiO_2$; $SrO \cdot SiO_2$	SiO_2	41,42
21	$CaO - SiO_2$	$2CaO \cdot SiO_2$; $3\ CaO \cdot 2\ SiO_2$; $CaSiO_3$	SiO_2	42,43
22	$MgO - SiO_2$	$2\ MgO \cdot SiO_2$; $MgO \cdot SiO_2$	SiO_2	43
23	$ZnO - SiO_2$	$2ZnO \cdot SiO_2$	SiO_2	43
24	$FeO - SiO_2$	$2FeO \cdot SiO_2$	SiO_2	44
25	$MnO - SiO_2$	$2\ MnO \cdot SiO_2$; $MnO \cdot SiO_2$	SiO_2	43
26	$Cu_2O - SiO_2$		SiO_2	45
27	$BaO - B_2O_3$	$3BaO \cdot B_2O_3$; $BaO \cdot B_2O_3$; $BaO \cdot 3\ B_2O_3$	$BaO \cdot 3\ B_2O_3$	43
28	$CaO - B_2O_3$	$3CaO \cdot B_2O_3$; $CaO \cdot 2B_2O_3$; $CaO \cdot B_2O_3$; $CaO \cdot 3B_2O_3$	$CaO \cdot 3\ B_2O_3$	43
29	$MgO - B_2O_3$	$3MgO \cdot B_2O_3$; $2\ MgO \cdot B_2O_3$; $MgO \cdot B_2O_3$	$MgO \cdot B_2O_3$	46
30	$ZnO - B_2O_3$	$5ZnO \cdot 2\ B_2O_3$; $ZnO \cdot B_2O_3$	$ZnO \cdot B_2O_3$	47
31	$CdO - B_2O_3$	$3CdO \cdot B_2O_3$; $2CdO \cdot B_2O_3$; $3CdO \cdot 2B_2O_3$; $2CdO \cdot 3\ B_2O_3$	$2\ CdO \cdot 3\ B_2O_3$	48
32	$PbO - B_2O_3$	$4\ PbO \cdot B_2O_3$; $2\ PbO \cdot B_2O_3$; $5PbO \cdot 4\ B_2O_3$; $PbO \cdot 2\ B_2O_3$	$PbO \cdot 2\ B_2O_3$	49
33	$CoO - B_2O_3$	$3CoO \cdot B_2O_3$; $2CoO \cdot B_2O_3$; $xCoO \cdot yB_2O_3$	$x\ CoO \cdot y\ B_2O_3$	50,51
34	$Na_2S - Ni_2S$	—	Ni_2S	8
35	$Na_2S - Ni_2S_3$	—	Ni_2S_3	18
36	$Na_2TiO_3 - K_2TiO_3$	$2\ Na_2TiO_3 \cdot K_2TiO_3$	$2\ Na_2TiO_3 \cdot K_2TiO_3$	52
37	$UF_6 - HF$	—	UF_6	53
38	see also $M^{I}Cl - M^{V}Cl_5$ systems			54

layers and also[55-58] the formation of complex compounds of the type nAX.mBX. In fact, as can be seen from Table 2, in most cases complex formation occurs as well as separation. Although these two phenomena would seem to be mutually exclusive (since the tendency to complex formation is known always to increase the mutual solubility of the components), the activity coefficient of a dissolved salt in systems exhibiting complex formation is always less than unity and, as Voskresenskaya[55] has shown, the real solubility curve (the primary crystallisation curve) lies below the ideal curve calculated from Shreder's equation[59].

On the other hand, it is also known that a "tendency" to separate into two phases (or actual separation) appears when the real solubility curve lies above the ideal curve, and the activity coefficient of the salt which crystallises is greater than unity in the melt. It is easily seen, however, that in the overwhelming majority of systems separation is a consequence of the complete or partial mutual insolubility not of the components AX and BX but of the compound nAX.mBX and the less polar component BX. The liquidus curves for several AX—BX systems show that separation occurs adjacent to the less polar components $AlBr_3$, $AlCl_3$, B_2O_3, and SiO_2. Between the heterogeneous region and the ordinate of the more polar component (NaBr, NaCl, KBr, KCl, CaO, MgO, BaO, etc.) one or more compounds of the type $A_n[B_mX_{nm}]$ appear. Part of the BX—$A_n[B_mX_{nm}]$ system can be regarded as an independent system of the AX—BY type having four different ions — A, B, X, and $[B_mX_{nm}]$. Thus the formation of complex compounds in AX—BX systems produces favourable conditions for separation owing to the nature of the anions. Actually the pair of anions X and $[B_mX_{nm}]$ satisfy all the conditions favouring separation enumerated in section I. It is also evident from Figs. 7—9 that in many AX—BX systems exhibiting complex formation and phase separation the temperature of the three-phase monotectic process is below the melting point of the complex compound, which makes it certain that separation is due to the mutual insolubility of the complex and BX, that the former does not dissociate into its components at the temperature at which separation occurs, and that one of the liquid phases consists mainly of the molten complex compound. The two liquid phases are here in equilibrium either with the solid compound $A_n[B_mX_{nm}]$, of its melting point is above that of the component BX, or with the solid BX phase, if the converse is true. Among real systems of the latter type are $AlBr_3$—AgBr, $-BaBr_2$, $-Hg_2Br_2$, $-SnBr_2$, and $-PbBr_2$, and $AlCl_3-BaCl_2$, $SrO-SiO_2$, $CaO-SiO_2$, $MgO-SiO_2$, $BaO-B_2O_3$, $CaO-B_2O_3$, $MgO-B_2O_3$, and $PbO-B_2O_3$.

In systems of this kind it quite often happens that the resulting complexes decompose on fusion into two immiscible liquids, one of which consists mainly of BX, and the other of either another complex compound or the component AX, if the latter is of low polarity. Representatives of the

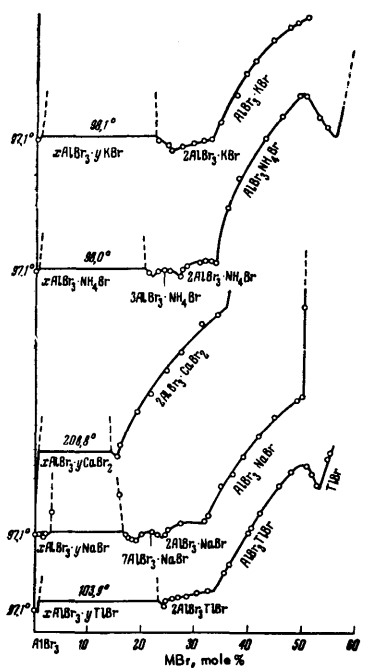


Fig. 7.

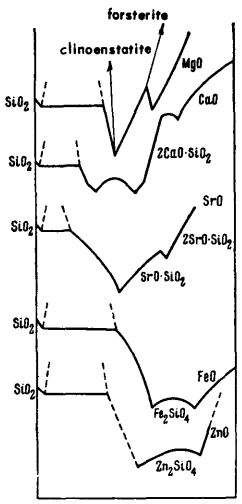


Fig. 8.

former are the systems $AlBr_3$–Na(K, NH_4, Tl, Ca)Br, $AlCl_3$–Na(K, Ag, NH_4, Tl)Cl, and CoO–B_2O_3, and the latter are represented by the $SnCl_2$–$SbCl_3$ system. Such systems are of interest firstly because they have hitherto been regarded as rare exceptions among metallic and organic systems[3], and secondly because the $SnCl_2$–$SbCl_3$ system provides a good example of conditions for the formation of two phases and of complexes being very similar: depending on the temperature, either two phases or a complex compound are formed. The complex $x SnCl_2.y SbCl_3$ exists only up to a temperature of 243.1°, when it decomposes into the immiscible components $SnCl_2$ and $SbCl_3$. The same type includes also a few silicate systems, e.g. FeO–SiO_2 and MnO–SiO_2, in which the compounds formed melt incongruently, without reaching the temperature at which immiscible liquids are formed.

On the above basis inorganic AX–BX systems which form two liquid layers can be classified as follows (Fig.10):

1. Systems formed by two non-saltlike compounds of low polarity, of either semi-closed or closed type (in Kossel's sense); the cations A and B bear three or more charges; no complex compounds are formed. Separation is a consequence of complete or partial mutual insolubility of AX and BX due to a sharp difference in the intermolecular cohesive forces in the components. The two liquid phases are in equilibrium with a solid phase formed by the higher-melting component. The $SbCl_3$–$SnCl_4$ system is an example.
2. Systems consisting of pairs of compounds AX and BX, one of which is like those in systems of group 1, while the other is saltlike, but the resulting cations do not have the inert gas type of electron shell, e.g. FeO, MnO, $SnCl_2$. The relative characteristics of the cations A and B favour both separation into two phases and complex formation, but the complexes formed melt (*a*) with decomposition, without reaching the temperature at which two phases are formed (FeO–SiO_2, MnO–SiO_2), or (*b*) with decomposition into two immiscible liquids ($SnCl_2$–$SbCl_3$). In both cases the solid phase in equilibrium with the two liquid phases consists of the higher-melting component.
3. Systems composed of pairs of compounds AX and BX, one of which is of the low-polarity type of $AlCl_3$, SiO_2, B_2O_3, etc., and the other is a typical salt of a uni- or bivalent metal or else an oxide of a bivalent metal. One or several complex compounds are formed in the systems. The formation of separate phases is here a consequence of the mutual insolubility of the complex and the low-polarity component; the two liquid layers are in equilibrium with a solid phase consisting of either the complex compound or the component BX, depending on their melting points. The complex compound in equilibrium with the two liquids either has the same composition in the liquid and solid state (Fig. 10, 3*a* and 3*d*) or else decomposes on melting into a complex of different composition and the component BX, when the solid and liquid phases of the compounds differ in composition (Fig. 10, 3*c*).

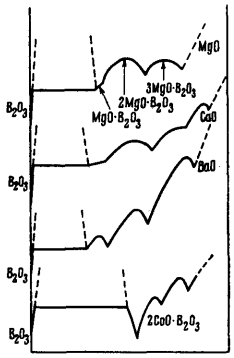


Fig. 9.

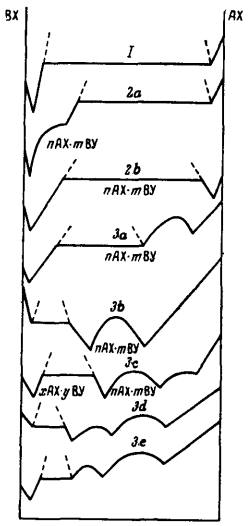


Fig. 10.

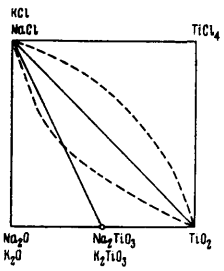


Fig. 11.

Somewhat different from these AX–BX systems is the $Na_2TiO_3-K_2TiO_3$ system, which contains the same anion and cations having very similar characteristics. According to Nisioka's data[60], two liquid phases are formed over the range 50–80 mole % Na_2TiO_3. According to the careful investigations of Sholokhovich[52], separation into two phases and compound formation both occur in this system.

This view of the formation of immiscible phases in AX–BX systems agrees with Esin's generally accepted hypothesis[1] of the microheterogeneity of liquids due to the formation, especially in silicate systems having low MO contents, of cybotactic groups approximating in composition to MO and to SiO_2. From electrostatic considerations and the shape of the property–composition diagrams, however, the cybotactic groups in silicate systems leading to microheterogeneity of the melt should evidently have a different composition. At low MO concentrations, where two liquid phases occur in silicate systems, cybotactic groups approximating to MO in composition are absent, since the oxygen of the MO is completely transferred to the silica, forming MSi_xO_y cybotactic groups; the part of the silica not required in the Si_xO_y ion forms cybotactic groups approximating to SiO_2 in composition. Formation of these groups determines the microheterogeneity of the melt and thus its separation into layers. A similar mechanism occurs also in $AlHal_3$–MHal systems.

III. AX–AY SYSTEMS

Table 3 lists the seventeen AX–AY systems known to us which form two liquid phases.

In the first two systems the separation has the same character as in AX–BX systems (Fig. 10, 3*c* and Fig. 11). The compounds $HCl.H_2O$ and $HBr.H_2O$ decompose on fusion into two immiscible liquids according to the equations

$$2(HCl.H_2O) = HCl.2H_2O + HCl,$$

$$2(HBr.H_2O) = HBr.2H_2O + HBr.$$

The two liquid phases are here in equilibrium with the compounds $HCl.2H_2O$ and $HBr.2H_2O$.

The remaining fifteen systems are composed of typical salts of sodium and potassium with various anions. In all these systems one of the salts is a silicate, titanate, or tetraborate. The fact that both components of these AX–AY systems (apart from the first two) are salts of the same alkali metal does not favour separation, but it does occur in these systems. How does it originate? Is it a consequence of the mutual insolubility of the components AX and AY due to a marked difference in properties of the anion pairs Cl and B_4O_7, SO_4 and B_4O_7, MoO_4 and TiO_3, SO_4 and TiO_3, etc., or of the formation of a complex compound immiscible with one component, or even because of these systems being unstable sections of more complex systems one of whose components is immiscible with the component AX? It is evidently necessary to take all three possibilities into account. But one of the components in all the systems (apart from 1 and 2) in Table 3 is an alkali-metal titanate, silicate, or tetraborate, which on fusion with other salts are converted into more acid or more basic forms; systems containing them are thus often unstable sections of more complex systems[64] and the third possibility is the most probable. In fact, as has already been shown, the $NaCl-Na_2B_4O_7$, $KCl-K_2B_4O_7$, and $Na_2SO_4-Na_2B_4O_7$ systems form subsections of the corresponding reciprocal ternary systems, and here the formation of immiscible liquids cannot be considered apart from these reciprocal systems (Fig. 5). Similarly, the $NaCl-Na_2TiO_3$ and $KCl-K_2TiO_3$ systems form unstable portions of the reciprocal ternary systems Na(K), Ti ‖ Cl, O, as is clear from Fig. 11.

TABLE 3.

1. $HCl - H_2O$[61]
2. $HBr - H_2O$[61]
3. $NaCl - Na_2B_4O_7$[75]
4. $KCl - K_2B_4O_7$[25]
5. $Na_2SO_4 - Na_2B_4O_7$[76]
6. $K_2WO_4 - K_2SiO_3$[62]
7. $KCl - K_2TiO_3$[63]
8. $NaCl - Na_2TiO_3$[63]
9. $K_2WO_4 - K_2TiO_3$[63]
10. $Na_2SO_4 - Na_2TiO_3$[63]
11. $K_2SO_4 - K_2TiO_3$[63]
12. $Na_2MoO_4 - Na_2TiO_3$[63]
13. $Na_2WO_4 - Na_2TiO_3$[63]
14. $K_2WO_4 - K_2TiO_3$[63]
15. $Na_2MoO_4 - Na_2SiO_3$[62]
16. $Na_2CrO_4 - Na_2TiO_3$[63]
17. $K_2CrO_4 - K_2TiO_3$[63]

Hence in seven of the seventeen AX–AY systems in Table 3 partial miscibility is associated either with complex formation (the first two) or with the systems representing unstable portions of more complex systems. In the remaining ten systems the origin of the separation has not yet been ascertained; it is evidently the same as in systems of chlorides with sodium and potassium tetraborates and titanates, and of sodium sulphate with sodium tetraborate.

CONCLUSION

This review leads to the following general propositions concerning the conditions necessary for immiscible liquid phases to be formed in inorganic systems:

1. All AX–BY, AX–BX, and AX–AY systems can form two liquids when both components are compounds of low polarity (halides, oxides, sulphides, etc.), examples being $SbCl_3-SnCl_4$ and TiO_2-SiO_2.[65]
2. All AX–BY, AX–BX, and AX–AY systems in which one component is a typical salt or a saltlike compound separate only when four different ions are present; when there is a sharp difference in characteristics between the cation pairs and the anion pairs; and when one component is a simple low-polarity compound like a halide or an oxide of a metal having 18 + 1 to 18 + 4 electrons in their outer shells (Ag, Pb, Tl), or even an acid anhydride such as B_2O_3, TiO_2, V_2O_5, etc. If the original components do not conform to these conditions, they may be established by interaction between the components.

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