

CCCLXVIII.—*The Influence of Dissolved Salts on the Mutual Miscibility Temperature of the Systems Ethyl Alcohol or Methyl Alcohol-Paraffins.*

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THE change of critical solution temperature (C.S.T.) of the system water-phenol caused by the addition of various salts has been described (Carrington, Hickson, and Patterson, J., 1925, 127, 2544). For the systems described below, with ethyl or methyl alcohol as the salt solvent, some modification was necessary in procedure.

*System 1. Ethyl Alcohol-Paraffin.*—The paraffin was a fraction of b. p. 160—180°. The alcohol was obtained by purifying and dehydrating 99.5% alcohol. The critical mixture (C.S.T. 33.5°) contained only 13% of alcohol. Instead of this a 50% mixture (by weight) was used in all cases. This mixture, the mutual miscibility temperature (M.M.T.) of which was 19.9°, was so hygroscopic that a blank M.M.T. was determined in each set of experiments. The highest reference temperature (used in the case of cadmium nitrate only) was 23.3°, representing a water absorption of 0.25%.

*System 2. Methyl Alcohol-Hexane.*—The hexane, b. p. 68—69°, was obtained by fractionally distilling petrol. The alcohol was shown to be practically water-free by means of Rothmund's solubility curve (*Z. physikal. Chem.*, 1898, 26, 433). The critical mixture (C.S.T. 42.0°) contained 20% of methyl alcohol and was too deficient in this component for convenient observation. The mixture used contained 50% of each component by weight and had an initial M.M.T. of 35.5°. Blank determinations were made as before in each set of experiments. The highest M.M.T., 40.5° (used in the case of zinc chloride), represents a water absorption of 0.4%.

All salts were prepared anhydrous. Experiments were carried out in stoppered tubes of thick glass so as to avoid evaporation and water absorption.

The results are stated in the tables in terms of the molecular concentration  $C$ , i.e., g.-mols. of salt per 1000 g. of *total alcohol and salt*;  $e$  is the elevation of M.M.T.; and  $E = e/C$ , the molecular elevation of M.M.T. In each case the value of  $e$  is shown above that of  $E$ . To facilitate comparison of the various systems, concentrations are expressed in terms of the salt solvent only. Values of  $e$  and  $E$  at even concentrations are obtained by interpolation from

separate curves; a bracketed number indicates slight extrapolation. The values for water, nearly identical in both systems, have been included.

*Values of  $e$  and  $E$ .*

*System 1.: Ethyl alcohol-paraffin.*

Salt.	Molecular concentrations.								
	0-02.	0-04.	0-06.	0-08.	0-10.	0-12.	0-16.	0-20.	0-24.
LiI	5.25° 255°	8.1° 197°	10.6° 175°	13.05° 163°	15.5° 154°	17.85° 148°	22.5° 139°	27.1° 136°	— (134°)
NaI	5.0 225	7.65 187	9.9 165	12.1 151	14.3 142	16.4 136	20.6 129	24.7 123	(28.7) (120)
NH <sub>4</sub> I	4.2 206	6.8 175	9.3 155	11.5 144	13.6 136	15.65 130	19.55 122	23.25 115	(27.0) (113)
KI	(3.65)	5.65	7.5	9.4	11.25	(13-15)	—	—	—
LiBr	(4.35) (215)	6.95 180	9.3 156	11.4 144	13.5 135	15.5 129	19.5 122	23.4 117	(27.3) (114)
NaBr	4.0 184	6.5 160	8.45 142	10.25 131	12.1 122	13.9 116	17.5 110	21.0 105	— (102)
NH <sub>4</sub> Br	(4.0)	6.45	8.4	10.2	12.0	13.65	16.75	19.7	(22.7)
LiNO <sub>3</sub>	(4.0)	6.6	8.75	10.8	12.75	14.55	18.0	21.45	24.9
LiCl	(4.0)	6.5	8.45	10.25	12.1	13.9	17.3	20.4	23.45
CH <sub>3</sub> ·CO <sub>2</sub> Na	(1.5)	159	142	131	122	116	108	102	97.5
	—	(2.75)	3.95	5.0	5.8	6.25	7.15	8.1	9.0
		(68.8)	65.6	64.0	59.0	53.0	44.8	40.2	37.2
	0.02.	0.06.	0.10.	0.16.	0.24.	0.30.	0.40.	0.50.	0.60.
FeCl <sub>2</sub>	(2.8)	6.5°	10.05°	15.3°	22.1°	26.95°	—	—	—
	—	107°	101°	96.0°	92.0°	89.9°	—	—	—
FeCl <sub>3</sub>	(2.0)	4.4	6.7	9.95	—	—	—	—	—
	—	74.0	68.0	62.0	—	—	—	—	—
CoCl <sub>2</sub>	(1.85)	4.8	7.35	10.95	15.55	18.9	(24.5)	—	—
	—	78.5	73.5	68.8	64.9	62.7	61.2	—	—
NiCl <sub>2</sub>	(2.1)	4.9	7.3	10.65	15.1	18.45	24.0	(29.55)	—
	—	82.0	73.0	67.2	63.0	61.2	59.8	(59.1)	—
CaCl <sub>2</sub>	(2.7)	5.3	7.65	11.2	16.1	19.8	26.0	—	—
	—	87.5	76.5	69.8	66.9	65.7	65.1	(65.0)	—
MgCl <sub>2</sub>	(1.6)	4.1	6.15	9.2	13.15	16.15	(21.15)	—	—
	—	67.5	62.5	57.5	54.2	53.3	(53.0)	—	—
ZnCl <sub>2</sub>	(1.0)	3.05	5.05	8.2	12.3	15.4	20.6	25.8	—
	(61.5)	51.5	51.5	51.4	51.4	51.4	51.5	51.6	—
CdCl <sub>2</sub>	1.3	3.25	(5.1)	—	—	—	—	—	—
	70.0	54.2	(51.2)	—	—	—	—	—	—
CdBr <sub>2</sub>	(1.5)	4.0	6.35	9.8	14.3	17.7	23.65	(29.7)	—
	(70.5)	66.2	63.5	60.8	59.5	59.4	59.2	(59.2)	—
CdI <sub>2</sub>	(1.3)	3.6	5.9	9.25	13.4	16.3	21.1	26.0	—
	(63.7)	61.7	60.0	57.7	55.2	53.6	52.2	52.0	(52.0)
Cd(NO <sub>3</sub> ) <sub>2</sub>	(2.45)	5.6	8.5	12.75	18.45	22.7	—	—	—
	—	92.0	85.0	79.4	76.8	76.8	—	—	—
CuCl <sub>2</sub>	(1.1)	3.0	4.45	6.6	9.4	11.65	15.3	19.0	22.8
	—	49.1	45.7	41.6	38.7	38.2	38.0	38.0	38.1
HgCl <sub>2</sub>	(0.2)	0.7	1.15	1.85	2.8	3.55	4.8	6.05	(7.3)
	—	(11.2)	11.2	11.3	11.4	11.6	11.9	12.3	(12.4)
HgBr <sub>2</sub>	(0.05)	(0.1)	0.1	0.1	0.1	0.1	0.4	0.9	(1.4)
	—	—	1.7	1.1	0.4	0.5	1.0	1.7	(2.4)
HgI <sub>2</sub>	-0.25	-0.75	—	—	—	—	—	—	—
	-12.2	-12.1	(-11.9)	—	—	—	—	—	—
Hg(CN) <sub>2</sub>	(0.8)	2.5	4.2	6.75	10.15	(12.7)	—	—	—
	(42.2)	42.2	42.2	42.2	42.3	(42.3)	—	—	—
Ca Butyrate	(0.6)	1.65	2.5	—	—	—	—	—	—
	—	27.6	25.0	—	—	—	—	—	—
Ca isoButyrate	(0.4)	1.1	1.65	—	—	—	—	—	—
	—	18.4	16.8	—	—	—	—	—	—
Water	(0.55)	1.55	2.45	3.8	5.5	6.7	8.65	10.65	12.65
	(26.4)	25.3	24.2	23.2	22.5	22.1	21.6	21.2	21.0

## System 2 : Methyl alcohol-hexane.

Salt.	Molecular concentrations.								
	0.02.	0.04.	0.06	0.08.	0.10.	0.12.	0.16.	0.20.	0.24.
NaI	(3.65°)	6.3° 155°	8.6° 142°	10.9° 136°	13.15° 132°	15.4° 129°	19.8° 124°	24.1° 121°	(28.2°) (117°)
KI	(3.9)	(6.45) (158)	8.85 147	11.2 141	13.5 136	15.7 131	20.0 125	(24.1) (120)	—
NH <sub>4</sub> I	(3.8)	6.45 161	8.85 149	11.2 141	13.5 136	15.65 130	19.65 123	23.5 118	27.35 114
LiBr	(4.0)	6.75 167	8.9 150	11.25 142	13.5 137	15.7 132	19.85 125	23.65 119	—
NaBr	(3.65)	6.3 158	8.6 144	10.75 134	12.9 128	15.0 125	19.0 118	22.65 113	(26.2) (109)
LiCl	(5.2)	(8.5) (215)	11.35 189	14.2 176	16.75 168	19.55 161	—	—	—
NaCl	4.8 242	—	—	—	—	—	—	—	—
LiNO <sub>3</sub>	(3.45)	(6.0)	8.1 135	10.1 126	12.1 121	14.05 117	17.8 111	21.4 107	25.1 104
FeCl <sub>3</sub>	0.02. (2.55°)	0.06. 6.7° 112°	0.10. 10.2° 103°	0.16. 15.15° 95.0°	0.24. 21.7° 90.0°	0.30. 26.6° 89.1°	0.40. —	0.50 —	0.60. —
FeCl <sub>2</sub>	(2.75)	6.9 116	10.75 109	16.0 99.7	21.9 91.5	—	—	—	—
CoCl <sub>2</sub>	(2.95)	6.95 115	10.5 105	15.6 97.2	21.45 89.1	—	—	—	—
NiCl <sub>2</sub>	(2.75)	6.65 111	10.1 102	15.0 94.0	20.8 86.9	—	—	—	—
CaCl <sub>2</sub>	(3.45)	8.2 136	12.25 122	18.2 114	25.95 108	—	—	—	—
MgCl <sub>2</sub>	(3.45)	8.1 136	12.35 123	18.7 117	(27.1) (113)	—	—	—	—
ZnCl <sub>2</sub>	(1.0)	2.95 —	4.9 50.5	7.9 49.9	12.0 49.4	15.2 49.9	20.55 51.2	—	—
CdCl <sub>2</sub>	1.85 93.0	(4.8) (79.0)	—	—	—	—	—	—	—
CdBr <sub>2</sub>	(1.25)	(3.9) (65.0)	6.5 64.5	10.3 64.0	15.45 64.0	19.25 64.0	25.7 64.4	—	—
CdI <sub>2</sub>	(1.25)	(3.8) (63.5)	6.35 63.5	10.2 63.5	15.35 63.5	19.35 63.7	26.1 (65.0)	—	—
Cd(NO <sub>3</sub> ) <sub>2</sub>	(2.5)	(6.9) (115)	11.0 109	16.8 105	(24.05) (100)	—	—	—	—
CuCl <sub>2</sub> †	(1.45)	(4.15) 89.0	6.6 66.5	10.1 63.2	14.7 60.8	18.9 60.2	23.9 59.7	—	—
HgCl <sub>2</sub>	(0.45)	(1.4) (24.5)	2.4 24.5	3.9 24.5	5.9 24.4	7.35 24.4	9.8 24.5	12.3 24.5	14.75 24.5
HgBr <sub>2</sub>	(0.25)	(0.85) (15.7)	1.4 15.4	2.3 14.8	3.45 14.4	4.35 14.5	5.85 14.7	7.4 14.9	—
HgI <sub>2</sub>	0.12 6.0	0.12 2.0	0.12 1.2	—	—	—	—	—	—
Hg(CN) <sub>2</sub>	(0.9)	(2.8) (47.5)	4.65 47.5	7.45 47.4	11.25 47.4	14.15 47.4	19.15 47.9	24.65 48.7	—
Water	(0.4)	(1.3) (22.4)	2.15 22.2	3.5 22.1	5.3 21.9	6.55 21.6	8.60 21.5	10.65 21.3	12.7 21.1

## Discussion.

Until the results obtained for numerous systems have been correlated it is sufficient to summarise the chief deductions from the behaviour of solutions of salts in ethyl and methyl alcohols. A strict comparison with, *e.g.*, the system water-phenol, cannot be made on account of the temperature differences and of the many salts practically insoluble in alcohol.

(i). The choice of the second liquid of the system (other than the salt solvent) is, *ceteris paribus*, immaterial to the results, provided, of course, that the salts are insoluble in it. Other cases will be

given later (compare the system methyl alcohol-carbon disulphide, Drücker, *Rec. trav. chim.*, 1923, 42, 552).

(ii). The ions may be arranged in the order of the effects they produce :

*System 1.*  $I > Br > NO_3 > Cl > \text{Butyrate} > \text{isoButyrate}$ .

$Li > Na > NH_4 > K > Ca > Co = Ni > Fe^{**} > Mg$   
 $> Zn = Cd > Cu > Hg^{**}$ .

*System 2.*  $Cl > I > Br > NO_3$ .

$Li > Na = K = NH_4 > Mg = Ca > Fe^{**} = Co = Ni$   
 $> Cd > Cu > Zn > Hg^{**}$ .

In system 1 the order of the univalent cations is nearly the same as, and in system 2 it is still nearer, that for aqueous solutions. (In the system water-phenol, lithium as the first member of a group was shown to be out of place in that it was intermediate between sodium and potassium. This is not so, however, at lower temperatures, *e.g.*, in the system water-butyric acid.) The order of the anions in (1) is nearly the reverse of that for aqueous solutions, and in (2) it is intermediate between that for aqueous solutions and that in (1).

(iii). In system 1 the effect of the anions is rather greater, and in system 2 it is much greater, than that of the cations. This applies also to aqueous solutions.

(iv). In system 1 univalent ions, especially cations, produce a greater rise than bivalent or trivalent ions. In system 2 ions carrying one and two charges have nearly the same effect, although the former still predominate. This is in marked contrast to aqueous solutions, where the effect of bivalent ions is double that of univalent.

In general, the magnitude of the effects discussed in (ii), (iii), and (iv) is in the order to be expected from, *e.g.*, the dielectric constants : water, methyl alcohol, ethyl alcohol.

(v). The tests of complexity or association in aqueous solution are applicable to alcoholic solutions.

In cases of normal solution there is a slight change in the variation of  $e$  with  $C$  (possibly due to change of solvation), which is accentuated in the change (decrease) of  $E$ . The lines obtained on plotting  $\log e$  against  $\log C$  for alcoholic solutions, however, are not quite straight.

Abnormality is shown by zinc, cadmium, and mercuric halides, mercuric cyanide, and water : in these cases the value of  $E$  is remarkably constant. Association is best shown by a comparison of curves ; thus, cadmium halides in each alcohol give very low values compared with those of the alkali halides, contrasted with cadmium nitrate relative to lithium nitrate ; nitrates being assumed to be normal in solution.

Since cadmium iodide gives about half the rise to be expected for the normal molecule, it is probably present in alcoholic solution mainly as  $Cd_2I_4$ . The association of the bromide and chloride is correspondingly less.  $E$  is constant and often negative when a solute is soluble in both phases (Duckett and Patterson, *J. Physical Chem.*, 1925, 29, 295). The negative values for mercuric iodide in both alcohols and the very small positive values for the bromide are accounted for by this fact, in addition to molecular association. The solubility of these mercuric salts in hexane and paraffin was verified experimentally. The other salts mentioned were insoluble in the second liquid, so that the low values may well be a measure of the association. The much higher value for mercuric cyanide, in contrast with other mercuric salts, is noteworthy.

In ethyl alcohol, the effect of ferric chloride is much greater than that of ferrous chloride; in methyl alcohol, it is slightly less. Ferric chloride is present in ethyl alcohol probably as  $FeCl_3$ , and this simple molecule may be partly associated in methyl alcohol.

The curve for sodium acetate has an inflexion at  $C = 0.10$ , indicating some alcoholysis.

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