Cryoscopic Studies on the Transition Points of the Compounds of Organic Solvents with Salts. III. The Congruent Melting Points of some Alcoholates of Alkali Halides.

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In previous papers⑴⑵ certain transition points at which the solid solvate melted to form the anhydrous salt and a solution saturated with this salt were cryoscopically studied and it was shown that this temperature was lowered by the addition of foreign substances according to the following relation,

$$\varDelta T = K\frac{100\,w}{WM}\ , \tag{1}$$

where $\varDelta T$ is the depression of the transition point, K the molecular depression referred to 100 g. of the pure solvent, w the weight of a foreign substance dissolved in W g. of the pure solvent and M the molecular weight of the foreign substance. The constant K referred to 100 g. of the pure solvent was preferred to that referred to 100 g. of the solvate corresponding to the experimental procedure.

In a number of systems there exists a congruent melting point at which a solid solvate melts completely and yields a liquid of the same composition as the crystalline solvate. This temperature may be also considered as a transition point for the alcoholate and its melt. The lowering of the congruent m. p. by the addition of foreign substances has been similarly investigated on the systems formed by alcohols and alkali halides: $LiCl–CH_3OH$, $LiCl–C_2H_5OH$, $LiBr–C_2H_5OH$, and $LiBr–n\text{-}C_3H_7OH$, and the results are given in the present communication.

The Solubilities of the Systems and the Congruent Melting Points. In the present systems the forms of the solubility curves exhibit a close parallelism to each other and the general type is shown by the diagrammatic curve in Fig. 1. The solubility curve of the alcoholate ABC possesses a retroflex region, represented in the figure by BC. The point B is the congruent m.p. The solubility of the anhydrous salt changes

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(1) H. Oosaka, this Bulletin, **3** (1928), 289.

(2) H. Oosaka, *Sci. Repts. Tokyo Bunrika Daigaku*, A, **1** (1933), 241.

only slowly with temperature and its curve CD cuts the curve ABC at the point C. This point is the transition or eutectic point for the alcoholate and the anhydrous salt.

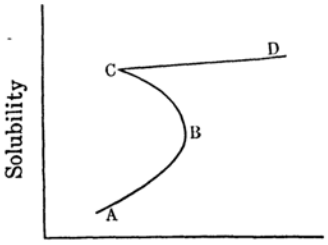

Fig. 1.

The system $LiCl-CH_3OH$. Simon⁽³⁾ observed the existence of the solid alcoholate $LiCl \cdot 3CH_3OH$. The solubility curve of the anhydrous salt was determined by Lloyd, Brown, Bonnell and Jones,⁽⁴⁾ and they described the transition point as 0.1°C. The solubility of the alcoholate had not been found so that the author made the preliminary determination and redetermined the solubility of the anhydrous salt.⁽⁵⁾ The results showed that the congruent m.p. (B in Fig. 1.) coincided approximately with the transition point (C in Fig. 1.) and was 12.9°C.

The system $LiCl-C_2H_5OH$. The solubilities of the alcoholate $LiCl \cdot 4C_2H_5OH$ and the anhydrous salt were determined by Turner and Bissett,⁽⁶⁾ the existence of the crystalline alcoholate being confirmed by them. Their solubility curve of the alcoholate possesses a retroflex portion, but they did not describe this behaviour. From their curve about 18°C. can be read as the congruent m.p. By the cryoscopic determination of the author this point was found to lie at 20.5°C.

The system $LiBr-C_2H_5OH$. Turner and Bissett⁽⁷⁾ observed the existence of the alcoholate $LiBr \cdot 4C_2H_5OH$ and Bonnell and Jones⁽⁸⁾ determined the solubility curves of the alcoholate and the anhydrous salt. The congruent m.p. was 23.8°C.

The system $LiBr-n\text{-}C_3H_7OH$. The solubilities of the system are not found in the literature, but the existence of the alcoholate $LiBr \cdot 4n\text{-}C_3H_7OH$ was confirmed by Turner and Bissett.⁽⁷⁾ The author determined preliminarily the solubilities and obtained the transition point as about 7°C., and the congruent m.p. as 35.8°C.

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(3) S. E. Simon, *J. prak. Chem.*, **20** (1879), 371.

(4) E. Lloyd, C. B. Brown, D. G. R. Bonnel and W. F. Jones, *J. Chem. Soc.*, **1928**, 658.

(5) The preliminary determination of solubility was carried out on the systems $LiCl-CH_3OH$ and $LiBr-n\text{-}C_3H_7OH$, but the results are not given here.

(6) W. E. S. Turner and C. C. Bissett, *J. Chem. Soc.*, **103** (1913), 1904.

(7) W. E. S. Turner and C. C. Bissett, *ibid.*, **105** (1914), 1777.

(8) D. G. R. Bonnel and W. J. Jones, *ibid.*, **1926**, 318.

Apparatus and Method of Procedure.

The apparatus used was similar to that already described.(2) A solution having the composition of the alcoholate was prepared from the pure alcohol and the anhydrous salt in a freezing-point tube with proper precaution against moisture. The tube was placed in the air-jacket immersed in a cooling bath at a temperature about 5°C. below the m.p. When the solution supercooled and the solid alcoholate commenced to separate out without induced by infection, the tube was transferred to the other air-jacket immersed in a thermostat at a temperature of 0.3–0.5°C. below the m.p. and the constant highest temperature was observed by a Beckmann thermometer. In certain cases, however, some crystals of the alcoholate were allowed to remain on melting the solid phase after each measurement and then used as nuclei for crystallisation in the following freezing. After the m.p. of the pure alcoholate was determined, a foreign substance was added into the solution and the same procedure was carried out. Since the molten alcoholate prepared was slightly turbid because of minute amounts of the suspended particles, centrifuging was in some cases applied to it. The clear solution thus obtained showed, however, the same result for the cryoscopic determination.

Preparation of Materials.

Alcohols. With the exception of ethyl alcohol these were dehydrated by aluminium amalgam.(9) The dehydration of ethyl alcohol was carried out by the method of Adickes,(10) using metallic sodium and ethyl formate.

Lithium chloride. Merck's salt was recrystallised from water as hydrate and was dehydrated by heating at 120–130°C.

Lithium bromide. This salt was prepared by the neutralisation of hydrobromic acid with lithium carbonate and then dehydrated at 130°C.

Other substances were purified by ordinary methods.

Experimental Results.

The system $LiCl$–CH_3OH. The solution of the composition $LiCl \cdot 3CH_3OH$ was liable to supercooling and the freezing commenced almost always at temperatures below −10°C., much lower than the congruent m.p. 12.9°C. Owing to this fact care was taken not to lose completely the crystalline alcoholate during the cryoscopic experiment.

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(9) R. F. Brunel, J. L. Crenshaw and E. Tobin, *J. Am. Chem. Soc.*, **43** (1921), 561.
(10) F. Adickes, *Ber.*, **63** (1930), 2753.

The molecular depressions for 100 g. of the pure alcohol were determined using water and acetone as solutes and the values 38 and 39 were obtained respectively.

The system LiCl–C_2H_5OH. The lowering of the congruent m.p. was measured for the following eight solutes and the constant K was calculated by the relation (1). The results are given in Tables 1 to 7.

Table 1. Solute: Water, mol. wt. = 18.

Weigt of alcohol W in g.	Weight of solute w in g.	Observed lowering of temperature ΔT in °C.	Molecular depression K
31.8	0.159	1.275	45.9
31.7	0.191	1.506	45.0
32.1	0.220	1.733	45.5
32.0	0.273	2.135	45.0
26.4	0.290	2.757	45.3

Mean: 45.3

Table 2. Solute: Acetone, mol. wt. = 58.

W	w	ΔT	K
31.8	0.346	0.851	45.4
25.7	0.347	1.059	45.5
31.9	0.452	1.102	45.1

Mean: 45.3

Table 3. Solute: Acetanilide, mol. wt. = 135.

W	w	ΔT	K
23.8	0.346	0.491	45.6

Table 4. Solute: Camphor, mol. wt. = 152.

W	w	ΔT	K
31.7	0.348	0.329	45.6
31.7	0.532	0.499	45.2
32.1	0.814	0.752	45.1

Mean: 45.3

Table 5. Solute: Carbon tetrachloride, mol. wt. = 154.

W	w	ΔT	K
31.7	0.765	0.690	44.0
31.3	0.886	0.803	43.7
31.8	0.971	0.864	43.6
33.1	1.459	1.271	44.4

Mean: 43.9

Table 6. Solute: Benzene, mol. wt. = 78.

W	w	ΔT	K
32.1	0.361	0.641	44.5
32.1	0.412	0.717	43.6
32.2	0.457	0.794	43.6
32.1	0.660	1.134	43.0

Mean: 43.7

Table 7. Solute: Toluene, mol. wt. = 92.

W	w	ΔT	K
31.9	0.320	0.481	44.1
32.6	0.470	0.674	43.0
32.5	0.694	0.989	42.6
31.6	0.675	1.004	43.2
31.6	0.715	1.046	42 5

Mean: 43.1

As shown in Tables 5 to 7 non-polar liquids give a little lower values for the constant K. This behaviour may be, as previously described,⁽²⁾ qualitatively interpreted as follows. The polarity of solute affects the activity of the solvent alcohol and thus on the dissolution of non-polar substances the decrease of this activity is smaller than in the case of polar solutes.

The system $LiBr-C_2H_5OH$. The molecular depression was determined quite similarly to the foregoing system. The supercooling was less than 1°C. The results are given in Tables 8 to 12.

Table 8. Solute: Water, mol. wt. = 18.

W	w	ΔT	K
31.1	0.046	0.493	60.0
31.6	0.078	0.778	56.8
31.8	0.200	2.023	57.9

Mean: 58.2

Table 9. Solute: Acetone, mol. wt. = 58.

W	w	ΔT	K
31.4	0.284	0.900	57.7
24.9	0.309	1.217	56.9

Mean: 57.3

Table 10. Solute: Benzoic acid, mol. wt. = 122.

W	w	ΔT	K
31.5	0.117	0.181	59.4

Table 11. Solute: Carbon tetrachloride, mol. wt. = 154.

W	w	ΔT	K
31.5	0.647	0.647	55.3
31.9	1.279	1.428	54.8

Mean: 55.1

Table 12. Solute: Benzene, mol. wt. = 78.

W	w	ΔT	K
31.4	0.245	0.553	55.3
31.5	0.446	0.992	54.7

Mean: 55.0

As shown in Tables 11 and 12 non-polar solutes give a little lower constants as in the foregoing system.

The system $LiCl-n-C_3H_7OH$. The equilibrium at the congruent m.p. was less stable in comparison with the other systems and the influence of supercooling was greater. Thus the results were somewhat irregular.

Table 13. Solute: Acetone, mol. wt. = 58.

W	w	ΔT	K
33.1	0.251	0.79	60.4
32.8	0.321	1.02	60.5
27.7	0.564	1.96	55.8

Mean: 58.9

Table 14. Solute: Water, mol. wt. = 18.

W	w	ΔT	K
33.1	0.122	1.10	53.7
25.3	0.211	2.48	53.5
32.8	0.293	2.76	55.6

Mean: 54.3

Table 15. Solute: Nitrobenzene, mol. wt. = 123.

W	w	ΔT	K
32.9	0.623	0.91	58.5
32.7	0.654	0.94	57.8

Mean: 58.2

The lower value for water cannot be explained only by these data. This will be discussed after more data are obtained.

Calculation of the Heat of Fusion from the Cryoscopic Constant.

It was shown before(1) that the molecular depression of the transition point at which a crystalline solvate melted to form the anhydrous salt and a saturated solution with regard to this salt could be expressed by the following equation,

$$K = \frac{RT^2}{H} \frac{nM_0}{100} \frac{c}{c+i}, \qquad (2)$$

where R denotes the gas constant, T the absolute transition point, H the heat of fusion per mol of the solvate, n the number of mols of the solvent per mol of the salt in the solvate, M_0 the molecular weight of the pure solvent, c the number of mols of the solvent per mol of the salt in the solution, and i the van't Hoff factor. This factor may be assumed as unity because of the high concentration and the previous result(11) of the vapour pressure determination of the similar system.

In the present case the molten solvate has the same composition as that of the solvate and c is equal to n. Therefore (2) becomes,

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(11) H. Oosaka, *Bull. Inst. Phys. Chem. Research* (Tokyo), **10** (1931), 466; Abstracts therefrom, **4** (1931), 48.

$$K = \frac{RT^2}{H}\frac{M_0}{100}\frac{n^2}{n+1}\,. \qquad (3)$$

Taking the probable value of the constant for polar solutes the heat of fusion was calculated and the results are given in Table 16.

Table 16.

Alcoholate	Congruent m.p. °C.	Molecular depression		Heat of fusion	
		K	$\overline{K}$	kcal. per mol	cal. per g.
$LiCl\cdot 3CH_3OH$	12.9	38	55	3.08	22.2
$LiCl\cdot 4C_2H_5OH$	20.5	45	55	5.60	24.7
$LiBr\cdot 4C_2H_5OH$	23.8	58	85	4.44	16.4
LiBr $4n$-C_3H_7OH	35.8	58	79	6.28	19.2

The values of the cryoscopic constant $\overline{K}$ referred to 100 g. of the solvate are also included in the table for referrênce. These were obtained by multiplication of K with $\overline{M}/nM_0$, $\overline{M}$ being the molecular weight of the solvate.

The Abnormal Molecular Depressions when Homologous Alcohols are dissolved as Foreign Substances.

When homologous alcohols were used as solutes in the cryoscopy, abnormally low values of the molecular depression were obtained. The results are given in Tables 17 to 27.

The system $LiCl$-CH_3OH.

Table 17.

Solute	W	w	ΔT	K
C_2H_5OH	24.6	0.601	1.76	33.1
n-C_3H_7OH	23.9	0.490	1.22	35.7
n-C_4H_9OH	23.9	0.336	0.69	36.3
iso-$C_5H_{11}OH$	23.1	0.462	0.82	36.1

The system $LiCl$-C_2H_5OH.

Table 18. Solute: Methyl alcohol, mol. wt. = 32.

W	w	ΔT	K
32.0	0.138	0.473	35.1
31.4	0.421	1.494	35.7
32.1	0.685	2.378	35.7

Mean: 35.5

Table 19. Solute: *n*-Propyl alcohol, mol. wt. = 60.

W	w	ΔT	K
32.1	0.479	0.713	28.7
22.7	0.469	0.953	27.7
31.5	0.660	0.972	27.8
31.9	0.822	1.190	27.7
31.1	0.990	1.534	28.9
24.6	0.914	1.677	27.1
25.0	1.124	2.108	28.1

Mean: 28.0

Table 20. Solute: *n*-Butyl alcohol, mol. wt. = 74.

W	w	ΔT	K
32.7	0.205	0.371	43.8
32.3	0.450	0.835	44.4
33.9	0.494	1.230	44.0
32.3	0.648	1.240	45.7

Mean: 44.5

Table 21. Solute: iso-Amyl alcohol, mol. wt. = 88.

W	w	ΔT	K
31.2	0.197	0.317	44.2
31.6	0.462	0.755	45.4
25.3	0.607	1.268	46.5
31.4	0.803	1.364	46.9
24.0	0.982	2.139	46.0

Mean: 45.8

The system LiBr-C_2H_5OH.

Table 22. Solute: Methyl alcohol, mol. wt. = 32.

W	w	ΔT	K
31.5	0.150	0.620	41.7
31.4	0.278	1.142	41.3

Mean: 41.5

Table 23. Solute: *n*-Propyl alcohol, mol. wt. = 60.

W	w	ΔT	K
23.7	0.433	0.430	14.1
25.0	0.648	0.648	15.0
31.4	1.040	0.789	14.3
31.4	1.172	0.917	14.7
21.9	0.936	0.971	13.6

Mean: 14.3

Table 24. Solute: iso-Propyl alcohol, mol. wt. = 60.

W	w	ΔT	K
32.3	0.416	0.689	32.1
31.8	0.473	0.774	31.2

Mean: 31.7

Table 25. Solute: *n*-Butyl alcohol, mol. wt. = 74.

W	w	ΔT	K
32.3	0.411	0.890	51.8

Table 26. Solute: iso-Amyl alcohol, mol. wt. = 88.

W	w	ΔT	K
25.7	0.361	0.889	55.7
31.5	0.473	0.983	57.6
24.3	0.613	1.659	57.9

Mean: 57.1

The system LiBr-*n*-C_3H_7OH.

Table 27.

Solute	W	w	ΔT	K
CH_3OH	26.5	0.481	2.70	47.6
C_2H_5OH	21.9	0.286	0.50	17.6
C_2H_5OH	32.1	0.861	1.06	18.2
n-C_4H_9OH	27.3	0.487	0.93	38.7
iso-$C_5H_{11}OH$	27.5	0.579	1.23	51.4

Consideration on the Anomalous Depression.

The results for the abnormal depression are summarized in Table 28.

Table 28.

Solute	Solvent			
	LiCl-CH_3OH	LiCl-C_2H_5OH	LiBr-C_2H_5OH	LiBr-C_3H_7OH
CH_3OH	Solvent	36	42	48
C_2H_5OH	33	Solvent	Solvent	18
n-C_3H_7OH	36	28	14	Solvent
iso-C_3H_7OH	—	—	32	—
n-C_4H_9OH	36	45	52	39
iso-$C_5H_{11}OH$	36	46	57	51
The normal value	38	45	58	58

It is clearly seen from the table that the anomaly becomes greater as the molecular weight of the solute alcohol approaches to that of the solvent alcohol. This anomaly may be accounted for by assuming that the solute alcohol forms a solid solution with the solid solvate, and can be formulated by considering vapour pressures of the system. In Fig. 2 the curves AC and BC show the vapour pressures of the pure solid alcoholate and its melt respectively, both dissociating to the anhydrous salt and alcohol vapour. The curve DE represents the vapour pressure of the solid solution and AE that of the liquid solution when a solute forming a solid solution is added to the system. The point C is the congruent m.p. of the pure alcoholate, E the m.p. of the solid solution, hence EF the depression of the m.p. ΔT, AD the depression of vapour pressure for the solid solution Δp_1, and AB that for the liquid solution Δp_2. If one mol of the solid solution contains n_1 mols of the solute alcohol and one mol of the liquid solution n_2 mols, then according to the Raoult's law

$$\Delta p_1 = n_1 p\,, \qquad \text{and} \qquad \Delta p_2 = n_2 p\,,$$

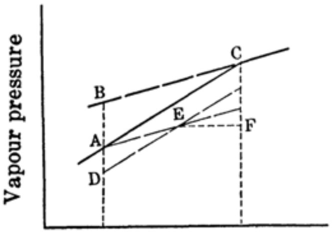

Fig. 2.

where p is the vapour pressure of the system at the m.p. Considering the geometrical relations of the figure over an infinitesimal range and applying the Clapeyron-Clausius equation the following relation is obtained,

$$n_2-n_1 = \Delta T\frac{q_1-q_2}{RT^2}\ , \tag{4}$$

where q_1 and q_2 are the molar heats of evaporation of alcohol from the alcoholate and the melt respectively. As the molar heat of fusion H can be represented by the following expression,(1)

$$H = n(q_1-q_2)\ ,$$

and hence (4) becomes

$$\Delta T = (n_2-n_1)\frac{nRT^2}{H}\ . \tag{5}$$

When the melt contains w g. of the solute alcohol per W g. of the solvent alcohol,

$$n_2 = \frac{M_0w}{WM}\left(\frac{n}{1+n}\right). \tag{6}$$

This relation is approximate but may hold within the experimental error because of the low concentration of the solute alcohol.

If r represents the partition coefficient of the solute alcohol between the liquid and solid solutions, and the solute has the same molecular weight in each phase,

$$r = n_1/n_2\ . \tag{7}$$

The constancy of the values of r can be seen from that of the values of K indifferent to the concentration. By using (6) and (7), (5) becomes

$$\Delta T = (1-r)\left(\frac{RT^2}{H}\frac{M}{100}\frac{n^2}{1+n}\right)\frac{100\,w}{WM}\ ,$$

where the term in the second brackets is the normal constant K already referred to. If the cryoscopic constant in the abnormal case is K', then

$$K' = (1-r)K\ .$$

In order to test this relation experimentally, tetra-alcoholate of lithium chloride as solvent and n-propyl alcohol as solute were chosen and the constant r was determined by measuring the concentrations of the solute alcohol in the liquid and solid phases in equilibrium, using a Zeiss water-interferometer. This experiment accompanied some difficulties on account of the similarity of the alcohols, the small concentration of the solute alcohol and the existence of salt in the solution, and besides the separation of both phases was not complete. The results were accordingly not very accurate but the value of r thus observed was in approximate accordance with the value calculated from the values K and K' which were in turn determined by the cryoscopic experiment.

Summary.

(1) The lowerings of the congruent melting points of the alcoholates: $LiCl \cdot 3CH_3OH$, $LiCl \cdot 4C_2H_5OH$, $LiBr \cdot 4C_2H_5OH$, and $LiBr \cdot 4n\text{-}C_3H_7OH$ by the addition of foreign substances have been measured and the molecular depressions referred to 100 g. of each alcohol have been determined.

(2) From these cryoscopic constants the heats of fusion of the alcoholates have been calculated.

(3) When homologues of the solvent alcohol have been used as solutes, abnormally low values have been obtained for the cryoscopic constant. This discrepancy may be considered as due to the formation of a solid solution between the alcoholate and the solute alcohol and this fact has been semi-quantitatively verified.

In conclusion the author expresses his hearty thanks to Professor M. Katayama for his continued interest and advice throughout this series of research. Thanks are also due to Professor I. Wada for giving to the author facilities for carrying out this work.

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