CRYOSCOPIC STUDIES ON THE TRANSITION POINTS OF THE COMPOUNDS OF ORGANIC SOLVENTS WITH SALTS. I.

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In the ordinary cryoscopy, we observe the univariant behaviour of systems of two components, a solvent and a solute. Similarly any univariant system formed of three or more components is also applicable to this purpose, and in analogy to the lowering of the freezing point of a single solvent, the lowering of the transition point by the addition of foreign substances was first investigated by Löwenherz⁽¹⁾ in the case of sodium sulphate decahydrate. He found that the transition point of the decahydrate into anhydrous salt, i. e. 32.38°C., was lowered by foreign substances by amount which gave 32.6 as the molecular depression referred to 100 gr. of the decahydrate. After this investigation similar studies were carried out for salt hydrates by other investigators⁽²⁾ in succession. Among them Dawson and Jackson state that "the referring of the concentration to 100 gr. of the solution in which the foreign substance is contained is a more convenient and correct procedure." In general, however, if a transition point of a salt hydrate at which it is transformed into an anhydride is to be used, the writer considers it more convenient to prefer the molecular depression referred to 100 gr. of water to that referred to 100 gr. of the molten hydrate or the solution. In the case of sodium sulphate, for example, since 322 gr. of the decahydrate contain 180 gr. of water, the constant referred to 100 gr. of water becomes $32.6 \times \frac{180}{322} = 18.2$, and the experiment may be carried out without using the molten hydrate.

This sort of cryoscopy can be applied also to the systems in which an organic liquid, instead of water, is present as solvent. In case an organic liquid with a strong solvent power has too low a freezing point to be used in the ordinary cryoscopy, this method would be convenient if the solvent combines with some salt to form a compound, of which transition point is in the neighbourhood of room temperatures. In this respect acetone comes in consideration first of all. This excellent solvent has its freezing point at -94.6°C., but forms some acetone compounds with salts, such as $NaI.3CH_3COCH_3$ [trans. pt. = 25.5°C.] and $HgCl_2 \cdot CH_3COCH_3$ [trans. pt. = 20.7°C.]. At the transition point these compounds are converted into the solid salt and the saturated solution. The results of the cryoscopic measurements carried out with these two systems are given in the following.

It is supposed that salt $[X]$ combines with n molecules of acetone to form acetone compound $[X. nA]$. In Fig. 1 curve (1) represents vapour pressures of the acetone compound dissociating to the salt and acetone vapour, and curve (2) vapour pressures of the system consisting of the salt, the

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(1) Löwenherz, *Z. physik. Chem.*, **18** (1895), 70.

(2) Van't Hoff & Dawson, *Z. physik. Chem.*, **22** (1897), 598; Van't Hoff & Müller, *Ber.*, **31** (1898) 2206; Morgan & Benson, *J. Am. Chem. Soc.*, **29** (1907), 1168; Morgan & Owen, ibid., 1439; Dawson & Jackson, *J. Chem. Soc.*, **93** (1908), 344.

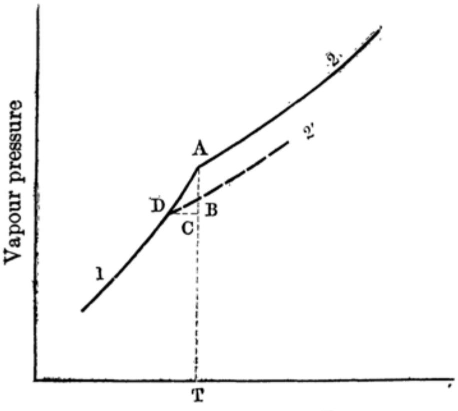

Fig. 1.

solution saturated with respect to the salt and acetone vapour. Curve (2′) shows vapour pressures of the system (2) when another solute is dissolved in it. Here it is assumed that the solute does not appreciably affect the solubility of the salt. A is the transition point, D the lowered transition point, DC the depression of the transition point (ΔT), and AB the depression of vapour pressure (Δp). Applying the Clapeyron-Clausius equation to this case, the following expression is derived for the depression ΔT,

$$\Delta T = \frac{RT^2}{q_1 - q_2} \frac{\Delta p}{p}, \quad \ldots \ldots \ldots \ldots \ldots (1)$$

where R is the gas constant, T the transition point, q_1 the molar heat of evaporation of acetone from the acetone compound and q_2 the molar heat of evaporation of acetone from the saturated solution. The changes which occur in these two kinds of evaporation may be shown by the following equations.

$$[\mathrm{X}.n\mathrm{A}] = [\mathrm{X}] + n\mathrm{A} - nq_1,$$

$$[\mathrm{X} + c\mathrm{A}] = [\mathrm{X}] + c\mathrm{A} - cq_2.$$

where [] represents a solid phase, ( ) a liquid phase, and a gaseous phase is shown by symbols only. The composition of the liquid phase is given by c, the number of mols of acetone which contains one mol of the salt. From these equations the expression for the melting of the compound is obtained.

$$[\mathrm{X}.n\mathrm{A}] = \frac{c-n}{c}[\mathrm{X}] + \frac{n}{c}(\mathrm{X} + c\mathrm{A}) - n(q_1 - q_2).$$

Now the molar heat of fusion H can be written as

$$H = n(q_1 - q_2). \quad \ldots \ldots \ldots \ldots \ldots (2)$$

If the concentration of the saturated salt solution and that of the same saturated solution which contains the other solute are given by N and N' in mole fractions, and the corresponding vapour pressures by p and p' respectively,

$$\text{then } \frac{p'}{p} = \frac{N'}{N}, \text{ accordingly } \frac{\Delta p}{p} = \frac{p - p'}{p} = 1 - \frac{N'}{N}.$$

If 100 gr. of acetone contains x gr. of the solute (mol. wt. $=M$),

$$N'=\frac{\frac{100}{58.05}}{\frac{100}{58.05}\left(1+\frac{i}{c}\right)+\frac{x}{\mathrm{M}}} \quad \text{and } N=\frac{\frac{100}{58.05}}{\frac{100}{58.05}\left(1+\frac{i}{c}\right)},$$

where i is the degree of dissociation of the salt in the solution plus unity and 58.05 is the molecular weight of acetone. Here also it is assumed that i and c are not appreciably affected by the existence of the solute. From the above relations follows

$$\frac{\Delta p}{p}=\frac{\frac{x}{\mathrm{M}}}{\frac{100}{58.05}\left(1+\frac{i}{c}\right)+\frac{x}{\mathrm{M}}}, \quad \ldots\ldots\ldots (3)$$

where x/M in the denominator may be neglected within the limits of experimental error.

Substituting equations (2) and (3) in equation (1), the following expression for the depression ΔT is obtained.

$$\Delta T=\frac{nRT^2}{H}\frac{\frac{x}{M}}{\frac{100}{58.05}\left(1+\frac{i}{c}\right)}.$$

If w gr. of the solute is present in W gr. of acetone,

$$\frac{x}{M}=\frac{100}{W}\frac{w}{M}.$$

Hence

$$\Delta T=\left(\frac{RT^2}{H}\frac{58.05}{100}\frac{nc}{(c+i)}\right)\frac{100}{W}\frac{w}{M}, \quad \ldots\ldots\ldots (4)$$

where the term contained in the outer brackets is independent of the nature of the solute and represents the molecular depression K of the transition point referred to 100 gr. of acetone.

Apparatus and Method of Procedure. A Beckmann⁽¹⁾ apparatus with a magnetic stirrer was used for the cryoscopic experiments. The cooling bath was kept constant within 0.1°, and the temperature was such that the convergent temperature was 0.1–0.2° below the transition point. To a known amount of acetone was added a sufficient amount of salt to form the satura-

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(1) Beckmann, *Z. physik. Chem.*, **44** (1903), 169.

ted solution and the solid phase, at a temperature one or two degrees above the transition point. The system was then supercooled, a crystal of the new phase, e. g. the acetone compound, was added and the constant maximum temperature was observed. The ordinary procedure of cryoscopy followed, and the molecular depression K was calculated by the expression (4): $\varDelta T = K\frac{100\,w}{W\,M}$, introducing the correction for x/M which was eliminated in equation (3).

Preparation of Materials. Acetone was dehydrated by K_2CO_3, and was distilled twice with precaution against moisture.

Sodium iodide was recrystallized from water as $NaI \cdot 2H_2O$ and was dehydrated by heating. Jones[1] describes that the solution of NaI in acetone was coloured deeply yellow. He supposed at first that this was due to the liberation of iodine but a test with starch paste showed that no free iodine was present, and consequently the yellow colour was ascribed presumably to some reaction between acetone and NaI. According to my experiment, however, the solution was colourless even when saturated and boiled. After some time this turned somewhat yellowish but not deeply yellow.

Mercuric chloride of the Japanese Pharmacopœia was used after drying without further purification.

Other substances were purified by sublimation or recrystallization.

Results. *The case of* $NaI.3CH_3COCH_3$. The lowerings of the transition point of this system caused by the addition of each of eight organic compounds were measured, and the results are given in the following table.

TABLE 1.

(1) Solute: Naphthalene (mol. wt. = 128).

Wt. of acetone (W) in gr.	Wt. of NaI in gr.	Wt. of solute (w) in gr.	Observed depression of trans. pt. ΔT	Molecular depression K
23.7	12.0	0.374	0.307	25.1
23.8	11.5	0.769	0.617	24.7
23.7	12.0	0.769	0.642	25.7
23.6	12.7	0.770	0.601	23.9
23.6	12.7	1.408	1.105	24.3
			Mean	24.7

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[1] Jones, *Am. Chem. J.*, **27** (1902), 21.

(2) Solute: Camphor (mol. wt. = 152).

W	Wt. of NaI	w	ΔT	K
23.8	11.7	0.585	0.366	22.8
23.7	12.7	0.585	0.369	22.9
23.8	11.7	1.275	0.793	22.8
23.7	12.7	1.275	0.787	22.6
23.8	11.7	1.659	1.025	22.8
			Mean	22.8

(3) Solute: Benzoic acid (mol. wt. = 122).

W	Wt. of NaI	w	ΔT	K
23.8	11.5	0.432	0.347	23.5
23.8	11.5	0.429	0.349	23.7
23.8	11.5	0.860	0.689	23.6
23.8	11.5	0.862	0.714	24.4
			Mean	23.8

(4) Solute: Acetanilide (mol. wt. = 135).

W	Wt. of NaI	w	ΔT	K
31.5	16.0	0.475	0.273	24.7
23.7	—	0.486	0.358	23.7
23.8	11.5	0.474	0.362	24.7
23.7	11.7	0.485	0.375	25.0
23.7	12.7	0.487	0.380	25.2
23.8	11.5	0.889	0.692	25.4
23.7	12.7	0.892	0.705	25.7
			Mean	24.9

(5) Solute: *p*-Nitranilne (mol. wt. = 138).

W	Wt. of NaI	w	ΔT	K
23.7	—	0.443	0.326	24.2
23.7	12.7	0.443	0.337	25.0
23.7	—	0.586	0.441	24.8
23.7	—	0.737	0.558	25.0
23.7	—	1.332	1.018	25.5
			Mean	25.1

(6) Solute: Phthalic anhydride (mol. wt. = 148).

W	Wt. of NaI	w	ΔT	K
23.8	11.5	0.529	0.346	23.3
23.7	11.5	0.528	0.349	23.4
23.8	11.5	1.055	0.687	23.3
23.7	11.5	1.054	0.691	23.4
			Mean	23.4

(7) Solute: Benzil (mol. wt. = 210).

W	Wt. of NaI	w	ΔT	K
23.8	11.5	0.682	0.302	22.3
23.4	11.5	0.665	0.312	23.2
23.7	11.5	0.682	0.323	23.7
23.8	11.5	1.081	0.488	22.8
23.7	12.7	1.081	0.501	23.3
23.4	11.5	1.074	0.509	23.5
23.7	11.5	1.081	0.511	23.8
			Mean	23.3

(8) Solute: Coumarin (mol. wt. = 146).

W	Wt. of NaI	w	ΔT	K
31.6	15.0	0.514	0.270	24.4
23.7	11.5	0.508	0.350	24.1
31.6	15.0	1.023	0.533	24.3
23.7	11.5	1.025	0.684	23.5
			Mean	24.1

The mean of these values of the molecular depression is 24.0. The value for each solute differs from the mean at most by amount of 5%, so that this system can practically be used for the cryoscopic measurment.

The values of the transition point obtained in these experiments are given in Table 2, where (I) is the readings of the Beckmann thermometer and (II) is the corresponding temperatures (corrected) in Celcius degree.

TABLE 2.

I	II	I	II	I	II	I	II
3.522	25.48	3.466	25.43	3.500	25.46	3.515	25.48
3.530	25.49	3.498	25.46	3.490	25.45	3.491	25.45
3.501	25.46	3.499	25.46	3.505	25.47	3.499	25.46
3.517	25.48	3.477	25.44	3.501	25.46	3.534	25.50
3.507	25.47	3.493	25.46	3.497	25.46	3.502	25.47
						Mean	25.46

This value is 0.2° lower than 25.7°C. obtained by other authors(1) from the solubility data.

The case of $HgCl_2 \cdot CH_3COCH_3$. Aten(2) gave 13°C. as the transition point of this compound, but according to the measurements similar to the previous case, this point is 20.7°C., 8° higher than the above value as shown in Table 3. Aten's value may be perhaps effected by the insufficiency of the solubility data used in the graphical determination of this point.

TABLE 3.

I	4.818	4.824	4.850	4.789	4.856	4.870
II	20.64	20.64	20.67	20.61	20.68	20.69

The mean: 20.66°C.

In this case if freezing and melting were repeated with the same solution it showed gradual lowering of the transition point, so that this cannot practically be used for the cryoscopic purpose. The acetone solution of $HgCl_2$ was at first colourless, but became yellowish in a few hours, deeply yellow in the next day, and it turned gradually from brown to a brownish black viscous liquid. The molecular depression was determined always using the solutions newly prepared. The results were not so concordant as in the case of sodium iodide. As the mean value of the molecular depression 24 was obtained.

Summary.

1. The lowering of the transition point, at which $NaI \cdot 3CH_3COCH_3$ loses acetone, by the dissolution of foreign substances has been studied and the molecular depression referred to 100 gr. of acetone has been determined

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(1) Macy & Thomas, *J. Am. Chem. Soc.*, **48** (1926), 1547. Wadworth & Dawson, *J. Chem. Soc.*, **129** (1926), 2784.

(1) Aten, *Z. physik. Chem.*, **54** (1906), 121.

as 24.0. The transition point has been also determined as 25.5°C. The method may be regarded as the cryoscopy using acetone with an artificially elevated melting point and can be used practically for the molecular weight determination.

2. A similar study has been carried out with $HgCl_2 \cdot CH_3COCH_3$. The molecular depression has been determined as 24 and the transition point as 20.7°C. This system shows, however, some inaccuracy so that it can hardly be applied to the practical cryoscopy.

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