Simple Estimates for Eutectic Behavior

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Abstract

A simple formula is derived for the eutectic point of an A-B system in terms of the monomer melting points and melting enthalpies. This estimate is tested on several non-ionic or ionic systems, with or without common ions, including choline chloride/urea mixtures. The results are compared with the Schröder-van Laar equation.

1 Historical Introduction

A textbook[1] expression for the freezing-point depression, ΔT, is

$$\Delta T = -K'_{\mathrm{A}} \, x_{\mathrm{B}}, \tag{1}$$

$$K'_{\mathrm{A}} = \frac{R(T^*_{\mathrm{A}})^2}{\Delta_{\mathrm{fus}} H_{\mathrm{A}}}, \tag{2}$$

where the fusion enthalpy $\Delta_{\mathrm{fus}} H_{\mathrm{A}}$ refers to the pure solvent, A, and $T^*_{\mathrm{A}} = T_{\mathrm{fus}}$ is its melting temperature at 1 bar. The molar fraction x_{B} refers to the solute, B. The expression (1) was published in 1878 by Raoult[2], the connections to $\ln x$ were made in 1884 by van't Hoff[3] and the Eq (2) was explicitly given by Riecke[4] in 1891, as mentioned by Preiss et al.[5]. In principle it is valid only for x near 0.

The idea of taking the melting curves[6, 7] from both ends and searching for a crossing[8] was already followed by van Laar and is commonly quoted as a 'Schröder-van Laar equation' (here 'S-vL'). For a biographical note on van Laar, see van Klooster[9]. Kordes[10] also quotes further independent discoveries by H. Le Chatelier and by A. Dahms. Findlay[11] cites Kordes. The textbooks of Kirkwood and Oppenheim[12], McGlashan[13] or Winn[14] mention the same idea. So does Heintz[15], who quotes van Laar. The equations are

$$T_{\mathrm{eut}} = T_{\mathrm{A}} \big/ \big[1 - \frac{R T_{\mathrm{A}} a_{\mathrm{A}}}{\Delta_{\mathrm{fus}} H_{\mathrm{A}}} \ln(1-x) \big] \tag{3}$$

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and

$$T_{\text{eut}} = T_{\text{B}}/\left[1 - \frac{RT_{\text{B}}a_{\text{B}}}{\Delta_{\text{fus}}H_{\text{B}}}\ln(x)\right], \tag{4}$$

respectively. The molar fraction x can also account for any dissociation, for ideal systems. For non-ideal systems, our constants a_{A} and a_{B} can be put $\neq 1$.

2 Theory: The Present Model

The simplest prediction for the eutectic point becomes for undissociated, ideal components

$$x_{\text{B,eut}} = \frac{T_{\text{A}}^* - T_{\text{B}}^* + K_{\text{B}}'}{K_{\text{A}}' + K_{\text{B}}'}, \quad T_{\text{eut}} = T_{\text{A}}^* - K_{\text{A}}' x_{\text{B,eut}}. \tag{5}$$

The same equation is used below for A:B salts with one common ion. For fully dissociated component A and undissociated B,

$$x_{\text{B,eut}} = \frac{T_{\text{A}}^* - T_{\text{B}}^* + 2K_{\text{B}}'}{K_{\text{A}}' + 2K_{\text{B}}'}, \quad T_{\text{eut}} = T_{\text{A}}^* - K_{\text{A}}' x_{\text{B,eut}}. \tag{6}$$

For the general case of an A:B eutectic where the two components have van't Hoff[16] factors i (number of particles that they yield upon dissociation or association), one obtains

$$x_{\text{B,eut}} = \frac{T_{\text{A}}^* - T_{\text{B}}^* + K_{\text{B}}' i_{\text{A}}}{K_{\text{A}}' i_{\text{B}} + K_{\text{B}}' i_{\text{A}}}, \quad T_{\text{eut}} = T_{\text{A}}^* - K_{\text{A}}' i_{\text{B}} \ x_{\text{B,eut}}. \tag{7}$$

For $i_{\text{A}} = i_{\text{B}} = 1$, Eq(7) reduces to Eq(5).

For non-ideal behaviour, we can also use the quadratic, virial-like fit

$$\Delta T = K_{A}' x_{\text{B}} + b_{\text{B}} x_{\text{B}}^2, \tag{8}$$

The K_{A}' is given by Eq (1).

Complete dissociation of the choline chloride (ChCl) into Ch^+ and Cl^- is assumed in Section 3.2. and no dissociation in Section 3.3.

3 Comparisons with experimental data

3.1 Salt mixtures

As a first application of Eqs(5-7), we use the primary data given in Table 1 to report in Table 2 the results on some binary salt mixtures, A-B.

We show for salts two examples, one good and one bad.

In the LiCl-NaCl case in Figure 1 the present model closely agrees with the experimental eutectic point. In the KCl-LiCl case in Figure 2, the experimental

Table 1: Properties of pure substances. 'Ox' = oxalic acid, 'EG' = ethylene glycol. '[DBNH] [OAc]' = 1,5-diazabicyclo[4.3.0]non-5-enium acetate, see Ostonen et al.[17]. It is one of the superbase-derived IL, tested for dissolving cellulose. The derivation of the ChCl values is explained by Fernandez et al.[18].

Substance	$\Delta_{\mathrm{fus}}H/\mathrm{kJ\ mol}^{-1}$	T^*/K	Ref.	K'_A/K
LiCl	19.8	883	[19]	327.4
NaCl	28.2	1075	"	341.2
KCl	26.3	1044	"	344.8
Na_2CO_3	29.7	1129	"	356.8
K_2CO_3	27.3	1172	"	419.0
Na_2SO_4	23.85	1157	"	466.7
K_2SO_4	36.6	1342	"	409.1
ChCl	4.3(6)	597(7)	[18]	689.2
		575	[20]	
[DBNH][OAc]	11.9(7)	318.2(2.0)	[17]	70.7
Urea	14.79	406(3)	[21]	92.7
Ox	-	464.45	[21]	-
EG	9.958	261(2)	[21]	56.9
Bi	11.106	544.6	[19]	222.0
Cd	6.21	594.2	[19]	472.7

results show strong non-linearities and agree with the prediction (5) at most qualitatively. Eq. (7) would give a nearly perfect agreement. Why this case is so non-ideal, is left for later study. For a better fit, see subsection 3.4. below. Further examples are mentioned in Table 2. The elemental Bi:Cd example there is quite adequate, cp. Winn[14].

3.2 Choline chloride/urea

The experimental points from the Figure 1 of Abbott et al.[20] are compared to Eqs (6) and (8) in present Figure 3. The data for the pure substances are given in Table 1. Note that the ChCl data appeared very recently[18]. Its K' value is the highest in Table 1. The fitted T_{eut} is not bad. The fitted parameters are given in the Table 3.

3.3 Other choline chloride systems

The choline chloride/oxalic acid melting curves are shown in Fig. 4 and again approximately follow the colligative limiting expressions. As a third example we give the predictions for choline chloride/ethylene glycol in Fig. 5.

Table 2: Predicted x_B and T_{eut} from Eq (5-7). Experimental values in parentheses.

A	B	x_B	T_{eut}/K	Comments
LiCl	NaCl	0.223	810	Eq (5).
		(0.28)	(827)	[a] Exp. [22].
LiCl	KCl	0.271	795	Eq (5).
		0.393	625	Eq (7)[b].
		(0.41)	(626)	[a] Exp. [22].
NaCl	KCl	0.548	886	Eq (5).
		(0.506)	(930)	Exp. [22].
Na$_2$SO$_4$	K$_2$SO$_4$	0.242	985	Eq (5).
		(0.258)	(1107)	Exp. [22].
Na$_2$CO$_3$	K$_2$CO$_3$	0.468	912	Eq (5).
		(0.4)	(983)	Exp.[23]
NaCl	K$_2$SO$_4$	0.286	779	Eq. (7)[c].
		(0.23-0.4)	840	Exp. [22].
KCl	K$_2$SO$_4$	0.271	766	Eq (7)[c].
		(0.26)	(963)	Exp. [22].
ChCl	Urea	0.430	300.5	Eq (6)
		(0.666)	(285)	Exp. [20]
ChCl	EG	0.560	210.9	Eq (6)
		(0.666)	(223.8)	Exp.[24]
Cd	Bi	0.609	409.4	Eq (5)
		(0.55)	417	Exp [14]

[a] A strongly non-ideal case[22].
[b] $i_A = i_B = 2$.
[c] $i_A = 2$, $i_B = 3$.

Table 3: The quadratic fits (8). The b_B is the fitting parameter.

A	B	b_B
ChCl	Urea	334.0
Urea	ChCl	-584.3
ChCl	Ox	230.2

3.4 Further fits

If one would use for KCl-LiCl the present Eq (7) with $i_A = i_B = 2$, nearly perfect agreement with experiment would result, see Table 2. Similarly, the Schröder-van Laar equations would give a nearly perfect agreement, see Figure 6.

4 Background and later applications

An estimate for the eutectic composition and temperature from monomer properties would be useful when searching for new potential systems. The work at our Department includes studies of dissolution of wood[25, 26] in ionic liquids (IL) and of the degree of the IL toxicity[27, 28].

The simple approaches discussed here, when applicable, will avoid the dynamic, electrostatical, and structural aspects, including the stoichiometries and the hydrogen-bond[29] formation. More detailed simulations of the phenomenon have been performed by the volume-based thermodynamic (VBT) approach[30], and the density functional theory (DFT)[31, 32], eventually with the COSMO solvent model[33, 5]. For a comparative assessment of all these, see Valderrama[34], who also discusses the experimental difficulties in determining the melting temperature, T_{fus}. Quantum chemical IL studies were reviewed by Izgorodina et al.[35].

Perhaps closest in spirit to the present Note is the discussion by Fernandez et al.[18]. For theoretical work note the COSMO study by Preiss et al.[5], who also provide a useful summary of the IL literature. Moreover, VBT thermodynamical models have been used for IL by Glasser and Jenkins[36] and by Mirarabrazi et al.[37]. For general reviews, see also Kirchner[38]. Zhang et al.[39], Smith et al.[24], the 2017 Faraday Discussion No. 206[40], the JCP IL issue edited by Perkin et al.[41], and the book by Marcus[42].

5 Conclusion

1) The key conclusion is that both the present equations and the earlier Schröder-van Laar equations Eq (3-4) can be useful tools for estimating eutectic behaviour. In such cases, the low eutectic points appear as just another colligative property, depending on the molar fraction, x.
2) While the 'Deep Eutectic Solvents (DES)' [43] are 'deep' in the sense that the eutectic points can lie much below the A-B line for ideal A:B mixtures,

$$\Delta T = - [x_A T_A^* + x_B T_B^*] + T_{eut}, \tag{9}$$

cp. Marcus' eq (7)[44], the present 'good' examples are not particularly deep compared to the normal freezing-point depression expressions. These examples include the Figures 1, 3, 5, and 7. In the sense that they are close to those colligative limits, the Deep Eutectic Solvents are not especially 'deep', an aspect

emphasized in Figure 8.

3) The eqs. (5-7) give estimates for the eutectic point, if $\Delta_{\mathrm{fus}}H$ and T^* of the individual components are experimentally known.

4) The examples in Fig. 3 give excellent fits to the single-parameter expression (8), see Table 3.

5) The Schröder-van Laar equations can give further improvement and are actually used in the applied chemistry literature. With the $a_{\mathrm{X}} = 1$ they still only involve the $\Delta_{\mathrm{fus}}H_{\mathrm{X}}$ and T_{X}^*. Take Kick et al.[45] as an example.

Conflicts of Interest

No conflicts of interest to declare.

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6   Keywords:

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