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A UNIFYING APPROACH TO THE THERMAL BEHAVIOR OF INCLUSION COMPOUNDS

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Abstract A rational approach to the understanding of the thermal stability of inclusion compounds requires an examination of all the involved phases, in particular the solid and the liquid phase. Equations for phase equilibria were derived within the framework of the regular solution theory: they contain the interaction parameter W which measures the tendency of solvent and solute to segregate. The shape of P-T and T-x diagrams changes dramatically with W, especially in cases where a miscibility gap in the liquid phase occur. On this basis it is possible to explain the behavior of the different host-guest systems such as urea- n alkanes and perhydrotriphenylene- n alkanes.

Thermodynamic properties of inclusion compounds have been studied from several points of view[1], but very little is known about their melting or decomposition with the formation of liquid phases, and about the interpretation of the behavior of different host-guest systems.

Data on P/T decomposition curves for urea and thiourea adducts were reported long time ago by Schlenk Jr[2] and by Redlich et al[3,4]. The melting or decomposition temperature of urea- n alkane inclusion compounds have also been reported[5].

The only host that has been extensively investigated in this respect is perhydrotriphenylene (PHTP), a tetracyclic saturated hydrocarbon $C_{18}H_{30}$. The melting diagram of the PHTP-polyethylene system[6] and the T/x and P/T diagrams of the PHTP- n heptane mixtures[7] were reported several years

ago.

The analysis of such diagrams has been performed under the hypothesis that ideal behavior occurs in the liquid phase[8]. An improved analysis has recently been reported in terms of the theory of regular solutions[9]; this approach was successfully tested for some significant guests of a hydrocarbon or non-hydrocarbon nature (cyclohexane, dioxan, etc)[10].

In this paper we aim to demonstrate how a few simple equations are able to predict and to interpret the thermal behavior of binary adducts (in particular of inclusion compounds) even in cases where the chemical nature of the two components is quite different. More precisely, we aim to show how the different stability of PHTP- and urea- n alkane inclusion compounds should be looked at not only in the properties of the solid phases but also in the repulsive host-guest interactions existing in the liquid state.

SOME EXPERIMENTAL POINTS

In spite of their many structural similarities the inclusion compounds formed by PHTP and linear hydrocarbons behave, as regards their thermal stability, solubility, rate of formation, etc., quite differently from the corresponding urea-hydrocarbon compounds. In particular, the urea adducts decompose at a temperature lower than the melting point of the pure host[5], while the corresponding PHTP adducts have a congruent melting point which depends on the length of the guest molecule and can be as high as 180°C [7,9,11], more than 50 K higher than that of the pure host (Table I).

A second point which drew our attention from the beginning was the different temperature and pressure ranges in which polymerization of monomers included in the crystal lattice of the two hosts could occur. As an example, butadiene can polymerize at room temperature and even at moderately higher temperatures when included in PHTP, whereas in urea low temperatures are required[13]. As inclusion is a prerequisite for polymerization[14], this fact is an indication of the lower stability of the adduct. According to Clasen[15] the highest temperature at which the butadiene - urea adduct can exist lies around - 27°C.

TABLE I

Melting or decomposition temperature of inclusion compounds containing n alkanes.

Number of C-atoms of the guest	PHTP (°C)	urea (°C)
7	120	42
8	124	-
10	131	81
12	136	91
14	141	102
16	145	108
18	148	114
20	151	118
24	153	125
28	156	131
32	160	-
36	161	-
∞ (polyethylene)	178	146
melting point of pure host	125	132

Data for urea - alkanes were taken from ref. 5, for urea-polyethylene from ref. 12.

It is interesting to compare the P-T diagrams of the PHTP - n heptane[8] and of the urea - n heptane systems, this latter taken from data reported by Schlenk Jr[2], (Figure 1a and 1b respectively). In the former case the range of stability of the adduct is extended toward higher temperatures and lower pressures. As reference points, the limit for existence of the urea adduct is 42°C, for the PHTP adduct, 120°C. At 20°C, the decomposition pressure is 19 mm Hg in the former case and less than 2 mm Hg in the latter. The condensed phase diagrams of the two systems are reported in Figs. 2 and 3. It would appear that all this could be attributed to a higher intrinsic stability of the PHTP adduct in terms of inclusion energy, due to a more favorable arrangement of host and guest molecules in the crystal phase. However this is not the case.

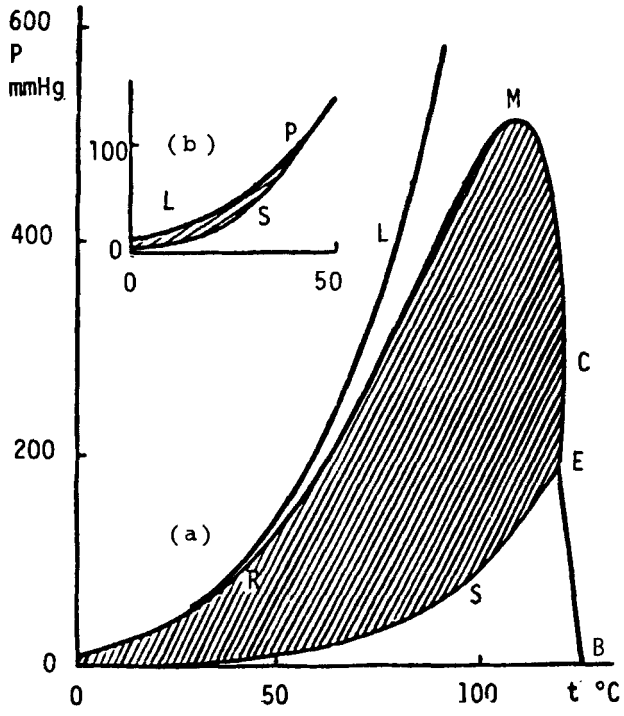

FIGURE 1. P-T projection diagrams of the PHTP-n-heptane (a) and the urea- n-heptane (b) systems. See ref. 22 for explanation of symbols. Shading shows existence region of inclusion compound.

Schlenk's data[2] were used to calculate a ΔH_{incl} value of -20.4 kJ mol^{-1} (-4.9 kcal mol^{-1}) for urea- n-heptane adduct: a value much greater than that measured in our laboratory for PHTP- n heptane adduct (-11.7 kJ mol^{-1} or -2.8 kcal mol^{-1})[8]. Measurement of ΔH_{incl} (= $-\Delta H_{dec}$) is obtained from the temperature dependence of the decomposition pressure according of the equation:

$$\ln(P/P_A) = -(\Delta H_{dec}/RT) + D' \qquad (1)$$

where P/P_A is the equilibrium constant of the reaction:

Inclusion Compound (cryst) $\rightleftarrows$ Guest (liq) + Host (cryst),

P_A and P are the vapor pressures of the pure liquid guest and of the included guest at the same temperature T and D' is a constant.

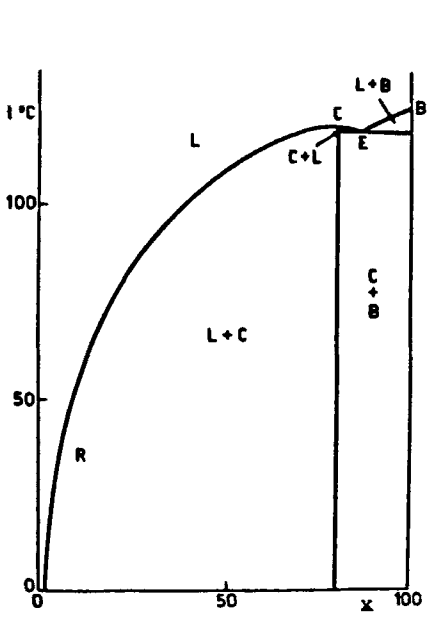

FIGURE 2. T-x diagram of the PHTP- n heptane system.

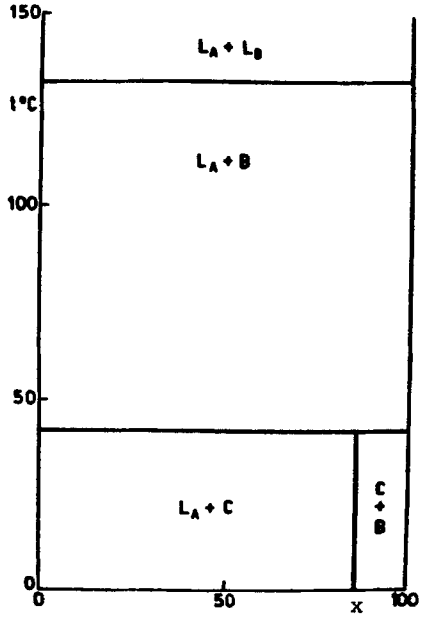

FIGURE 3. T-x diagram of the urea- n heptane system.

x = mole fraction of host

This contradiction prompted us to look for an explanation of the phenomenon in a different direction. In fact, the location of a phase transition is the result of a balance of the properties of all the phases involved, solid, liquid and vapor. In the present case, attention should be directed mainly to the nature of the liquid phase which occurs after the melting or the decomposition of the inclusion compound. This problem has already been discussed by us on a qualitative basis on several occasions[9,16,17]. We now propose a quantitative description.

A THERMODYNAMIC APPROACH

In a series of papers[8-10] we demonstrated that the solubility curve of PHTP adducts in the presence of an excess of either the host or the guest component is expressed by equation (2), first proposed by Prigogine for crystalline racemic compounds[18] and put in a more general form by Haase[19]:

$$\ln(x_A/x_{oA}) + n \ln(x_B/x_{oB}) = -(\Delta H_C/R)(1/T - 1/T_C) \qquad (2)$$

where x_A and x_B are the molar fractions of guest and host in the solution, x_{oA} and x_{oB} are the mole fractions in the inclusion compound, $n = x_{oB}/x_{oA}$, T_C and ΔH_C are the melting temperature and the melting enthalpy (referred to one mole of guest and supposed to be constant with temperature) of the pure adduct.

This equation is valid under the following conditions: complete decomposition of the adduct in the liquid phase, instability of the "empty" channels in the solid inclusion compounds, immiscibility of the two crystal phases (pure host and inclusion compound). If we substitute x for x_B, 1 - x for x_A and express x_{oA} and x_{oB} in terms of n, equation 2) converts into (3):

$$\ln(1-x) + n \ln x = Q - (\Delta H_C/R)(1/T - 1/T_C) \qquad (3)$$

where $Q = n \ln n - (n + 1) \ln (n + 1)$

For a volatile guest and a non-volatile host the same curve is expressed in the P-T projection diagram by equation (4):

$$\ln(P/P_A) + n \ln(1-(P/P_A)) = Q - (\Delta H_C/R)(1/T - 1/T_C) \qquad (4)$$

The decomposition pressure of mixtures of inclusion compound and pure host follows equation (5):

$$\ln P = -(\Delta H_v/RT) + D \qquad (5)$$

where ΔH_v refers to one mole of guest in the reaction:

$$\text{Inclusion Compound (cryst)} \rightleftarrows \text{Host (cryst)} + \text{Guest (vapor)}$$

and D is a constant which contains the coordinates of the quadruple point. This point is thermodynamically invariant because of the presence of four phases (vapor, liquid, crystalline inclusion compound and pure crystalline host). Depending on the circumstances it corresponds to a eutectic (Fig. 1a) or to a peritectic point (Fig. 1b). ΔH_v and ΔH_{dec} (see equation (1)) differ by a quantity equal to the vaporization heat of pure liquid guest.

To complete the description of the phase diagrams a further equation concerning the solubility curve of crystalline host in host-guest liquid mixtures should be introduced:

$$\ln(1-(P/P_A)) = \ln x = -(\Delta H_B/R)(1/T-1/T_B) \qquad (6)$$

where T_B and ΔH_B are the melting temperature and the melting enthalpy of the pure crystalline host.

The above equations hold true when the host-guest liquid mixture behaves as an ideal solution. For real solutions activity should replace mole fraction and equations (2), (3), (4) and (6) should be modified. Within the scheme of regular solutions we can express the activity coefficient γ_i as a function of composition and of an interaction parameter W, assumed, in a first approximation, to be independent of temperature and composition[20]:

$$\ln \gamma_i = (W/RT)(1-x_i)^2 \qquad (7)$$

Accordingly, equations (3) and (6) convert into (8) and (9), respectively:

$$\ln(1-x) + n \ln x = Q - (\Delta H_C/R)(1/T-1/T_C) - (W/RT)(x^2+n(1-x)^2-(n/(n+1))) \qquad (8)$$

$$\ln x = -(\Delta H_B/R)(1/T-1/T_B)-(W/RT)(1-x)^2 \qquad (9)$$

Validity of equations (8) and (9) and methods for evaluation of W from P/T curves are discussed elsewhere[10]. In the present discussion we examine the liquid phase further.

It is known that a miscibility gap occurs in a liquid system when the interaction parameter W exceeds $2RT$[20]. Assuming the hypothesis of equal molecular volumes for host and guest (this assumption permits an analytical solution to the problem, but is not conceptually necessary), the L_1-L_2 curve in the T-x diagram is represented by equation (10)[21]:

$$\ln((1-x)/x) = (W/RT)(1-2x) \qquad (10)$$

In the absence of a specific interaction, e.g. hydrogen bonding, parameter W is positive and measures the tendency of solvent and solute to segregate. It has a twofold influence on the phase diagrams: it modifies the shape of curves R-C-E and B-E (and consequently changes the position of point E) and generates the miscibility gap. The liquid-liquid curve can intersect the solid-liquid diagram and can alter the field of existence of the corresponding phases in a significant way.

RESULTS AND DISCUSSION

The condensed phase diagram of a hypothetical AB_3 inclusion compound (or more generally of a AB_3 crystalline adduct) has been calculated according to equations (8)-(10), for the following values of W/R: 0, 400, 900, 2000 K. ΔH_C, ΔH_B, T_C and T_B were kept constant for all calculations: $\Delta H_C/R$ = 10000 K; T_C = 400 K; $\Delta H_B/R$ = 2000 K; T_B = 400 K. Our results are reported in Figure 4, a-d.

The ideal case (Fig. 4a) looks very like the experimental PHTP- n heptane diagram (see Fig. 2). Fig. 4b shows some modification of the solubility curve, which changes its slope especially at low host concentration and becomes almost horizontal. In Fig. 4c, a liquid-liquid separation occurs at temperatures higher than T_C. The value of W is such that intersection of the L_1 -L_2 curve with the solid-liquid diagram occurs between C and E. The inclusion compound no

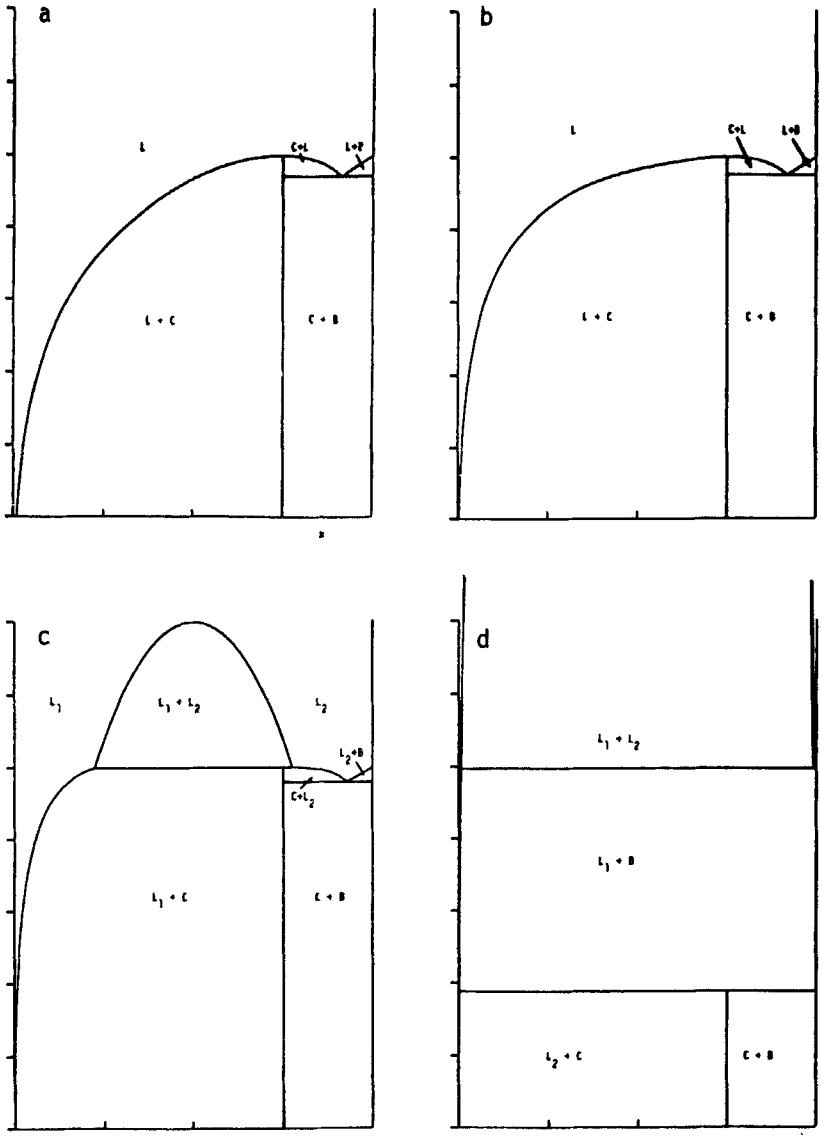

FIGURE 4. Calculated T-x diagrams for a hypothetical AB_3 inclusion compounds. W/R = 0, 400, 900, 2000 K respectively.

longer has a congruent melting point, but decomposes into two liquid phases at a temperature between T_E and T_C.

A further increase of W shifts the intersection point between E and B (Fig. 4d). We point out that even in the left-hand side of the diagram intersection occurs between the L_1-L_2 curve and the solubility curve of pure host (equation (9)) and not with that of the inclusion compound (equation (8)). Under these conditions, the inclusion compound cannot exist. Its highest temperature of existence (i.e. its decomposition point) is determined by the intersection of the liquid-pure host equilibrium curve with that of the liquid - inclusion compound which occurs at a temperature lower than T_B. After decomposition the system consists of a liquid phase (very rich in the guest or, in the limiting case, consisting of the pure guest) and the pure crystalline host.

Once the termodynamic parameters of the solid phases are defined, the decomposition point of the inclusion compound depends on the W value only. For a host-guest system in which the components have very little compatibility (high W value) we can predict a low stability for the inclusion compound.

We arrived at this conclusion by comparing the behavior of a series of guests with the same host. It seems quite legitimate to apply the same treatment to the examination of behavior of two hosts with the same guest. In the case we are interested in, the system PHTP- n alkane has a low or null W value, whereas for urea and n alkanes, due to their reciprocal insolubility, we can predict very high W values. In order to verify the general application of our results, we performed calculations with different ΔH_C and T_C values: the results, not reported here, are completely consistent with those discussed above. Other calculations were carried out with regard to the P-T diagrams. In this case too, a progressive reduction of the existence region of the adduct toward low temperatures and higher pressures was observed when increasing W.

Appearence of a peritectic point P, instead of the eutectic, occurs when intersection of the vapor-solid C-solid B curve with the vapor-liquid-solid curves occurs at a pres-

sure higher than that corresponding to C. When host and guest are almost insoluble, point P is placed on the vapor pressure curve of the pure guest. The two diagrams shown in Fig. 1a and 1b pertaining to the PHTP- n heptane and urea- n heptane systems correspond exactly to those predicted for nearly ideal and strongly non-ideal systems.

REFERENCES

1. N. G. Parsonage and L. A. K. Staveley, in Inclusion Compounds, edited by J. L. Atwood, J. E. D. Davies and D. D. MacNicol (Academic Press, London, 1984), vol. 3, chapt. 1, pp. 1 - 36.
2. W. Schlenk Jr., Justus Liebigs An. Chem., 565, 204 (1949).
3. O. Redlich, C. M. Gable, A. K. Dunlop and R. W. Millar, J. Am. Chem. Soc., 72, 4153 (1950).
4. O. Redlich, C. M. Gable, L. R. Beason and R. W. Millar, J. Am. Chem. Soc., 72, 4161 (1950).
5. H. G. McAdie, Can. J. Chem., 40, 2195 (1962).
6. M. Farina, G. Allegra and G. Natta, J. Am. Chem. Soc., 86, 516 (1964).
7. M. Farina, G. Di Silvestro and M. Grassi, Makromol. Chem., 180, 1041 (1979).
8. M. Farina and G. Di Silvestro, J. Chem. Soc., Perkin Trans. 2, 1406 (1980).
9. M. Farina, in Inclusion Compounds, edited by J. L. Atwood, J. E. D. Davies and D. D. MacNicol (Academic Press, London, 1983), vol. 2, chapt. 3, pp. 69 - 95.
10. M. Farina and G. Di Silvestro, manuscript in preparation.
11. G. Allegra, M. Farina, A. Immirzi, A. Colombo, U. Rossi, R. Broggi and G. Natta, J. Chem. Soc. (B) 1020 (1967).
12. F. Monobe and F. Yokoyama, J. Macromol. Sci., Phys., 8, 295, (1973).
13. D. M. White, J. Am. Chem. Soc., 82, 5678 (1960).
14. M. Farina, G. Audisio and M. T. Gramegna, Macromolecules, 4, 265 (1971).
15. H. Clasen, Z. Elektrochem. 60, 982 (1956).
16. M. Farina and G. Di Silvestro, Gazz. Chim. Ital. 112, 91 (1982).

17. M. Farina, G. Di Silvestro and P. Sozzani, Mol. Cryst. Liq. Cryst. 93, 169 (1983).
18. I. Prigogine and R. Defay, Chemical Thermodynamics, translated by D. H. Everett, Longmans Green, London, 1954, p. 375.
19. R. Haase, Thermodynamik der Mischphasen, Springer Verlag, Berlin, 1956, p. 429.
20. E. A. Guggenheim, Mixtures, Oxford Press, Oxford, 1952.
21. see ref. 19, p. 421.
22. Explanation of symbols:
B: host; E: eutectic point; C: inclusion compound; L: liquid; P: peritectic point; M: maximum pressure point; S: generic point on the solid-vapor curve; R: generic point on the saturated solution curve.