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# Estimation of Enthalpies of Fusion, Melting Temperatures, Enthalpies of Transition, and Transition Temperatures of Pure Compounds from Experimental Binary Solid−Liquid Equilibrium Data of Eutectic Systems

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This paper presents a procedure for the estimation of enthalpies of fusion, melting temperatures, enthalpies of transition, and transition temperatures using experimental binary solid−liquid equilibrium data of eutectic systems and the group contribution method modified UNIFAC (Dortmund) for the calculation of the required activity coefficients. Additionally, experimental solid−liquid equilibrium data of the system tetrachloromethane + *m*-xylene are presented.

## Introduction

Enthalpies of fusion and transition as well as their corresponding temperatures are pure component properties of great interest. For instance, they are needed for the prediction of solid−liquid equilibria (SLE), which form the basis for any crystallization process. And furthermore, SLE data are important considering pipeline and reactor design, where undesired crystallization leads to safety risks.

Despite their wide range of application, expensive and time-consuming calorimetric measurements are necessary to determine $\Delta_{\mathrm{fus}}H_i$ and $\Delta_{\mathrm{trs}}H_i$. In contrast to this, it is rather easy to determine binary solid−liquid equilibria (Jakob et al., 1995).

In this paper a procedure is introduced that describes the estimation of the mentioned pure component properties by using binary solid−liquid equilibrium data and the group contribution method modified UNIFAC (Dortmund) (Gmehling et al., 1993).

For eutectic systems an equation for solid−liquid equilibria can be derived starting from the isofugacity criterion (Gmehling and Kolbe, 1992). After some useful simplifications (neglecting the temperature dependence of the molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_i$, neglecting the difference between the molar heat capacity of the liquid $c_{\mathrm{P},i}^{\mathrm{L}}$ and solid $c_{\mathrm{P},i}^{\mathrm{S}}$, etc.), the following equation is obtained (Jakob et al., 1995)

$$\ln x_i^{\mathrm{L}}\,\gamma_i^{\mathrm{L}} = -\frac{\Delta_{\mathrm{fus}}H_i}{RT}\cdot\left(1-\frac{T}{T_{\mathrm{fus},i}}\right) - \frac{\Delta_{\mathrm{trs}}H_i}{RT}\cdot\left(1-\frac{T}{T_{\mathrm{trs},i}}\right) \quad (1)$$

where $x_i^{\mathrm{L}}$ is the mole fraction of component *i* in the liquid phase, $\gamma_i^{\mathrm{L}}$ the activity coefficient of component *i* in the liquid phase, $\Delta_{\mathrm{fus}}H_i$ the molar enthalpy of fusion of component *i*, $T_{\mathrm{fus},i}$ the melting temperature of component *i*, $\Delta_{\mathrm{trs}}H_i$ the molar enthalpy of transition of component *i*, $T_{\mathrm{trs},i}$ the transition temperature of the solid−solid transition of component *i*, *T* the absolute temperature, and *R* the universal gas constant.

If solid−solid transition does not occur below the melting point of the pure component, the last term in eq 1 can be neglected and eq 1 simplifies to (Gmehling et al., 1978)

$$\ln x_i^{\mathrm{L}}\,\gamma_i^{\mathrm{L}} = -\frac{\Delta_{\mathrm{fus}}H_i}{RT}\cdot\left(1-\frac{T}{T_{\mathrm{fus},i}}\right) \quad (2)$$

In this paper eqs 1 and 2 are used in order to estimate the pure component data from experimental binary SLE data.

For the first attempt to solve this problem, the following simplifications were made:

For the mole fractions $0.95 \le x_i^{\mathrm{L}} \le 1$, the real behavior of the mixture can be neglected, and the activity coefficient is near unity ($\gamma_i^{\mathrm{L}} \approx 1$). Then eq 2 can be rewritten as

$$\Delta_{\mathrm{fus}}H_i = -\frac{\ln x_i^{\mathrm{L}}}{\left(1-\frac{T}{T_{\mathrm{fus},i}}\right)}\cdot RT \quad (3)$$

The results obtained were only satisfying for nearly ideal systems. For mixtures showing real behavior, the activity coefficient must be considered. A transformation of eq 2 leads to

$$\ln x_i^{\mathrm{L}}\,\gamma_i^{\mathrm{L}} = -\frac{\Delta_{\mathrm{fus}}H_i}{R}\cdot\frac{1}{T} + \frac{\Delta_{\mathrm{fus}}H_i}{R\cdot T_{\mathrm{fus},i}} \quad (4)$$

The plot of $\ln x_i^{\mathrm{L}}\,\gamma_i^{\mathrm{L}}$ against $1/T$ produces a linear plot. It is possible to obtain $\Delta_{\mathrm{fus}}H_i$ from the slope ($-\Delta_{\mathrm{fus}}H_i/R$) and $T_{\mathrm{fus},i}$ from the axis intersection ($\Delta_{\mathrm{fus}}H_i/R\cdot T_{\mathrm{fus},i}$) by linear regression.

Plesnar and Bylicki (1993) have taken into account the real behavior by applying different $g^{\mathrm{E}}$ models (Wilson, NRTL, and UNIQUAC). In this paper the activity coefficient $\gamma_i^{\mathrm{L}}$ is calculated with modified UNIFAC (Dortmund). This means that no additional experimental information is required.

## Results

***I. Estimation of the Molar Enthalpy of Fusion $\Delta_{fus}H_i$ and the Melting Temperature $T_{fus,i}$.*** For the first test, systems with known enthalpies of fusion and melting temperatures for both components were selected. All experimental data (binary SLE data and pure component properties) were taken from the Dortmund Data Bank (DDB) except otherwise noted.

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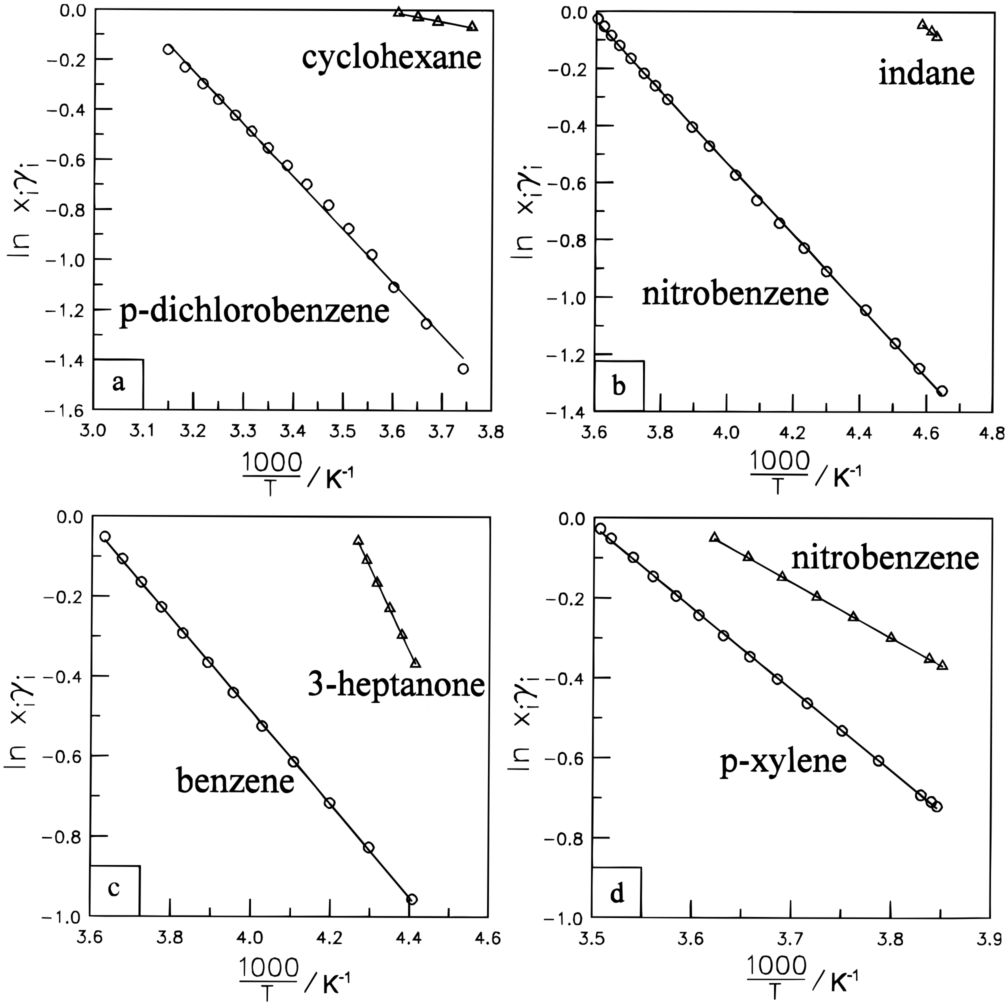

**Figure 1.** Plots for systems containing components with known enthalpy of fusion and melting temperature: (a) *p*-dichlorobenzene + cyclohexane (Serna et al., 1969); (b) indane + nitrobenzene (Jakob et al., 1995); (c) 3-heptanone + benzene (Fiege, 1996); (d) *p*-xylene + nitrobenzene (Proust, 1986).

**Table 1. Estimated Pure Component Properties Using Linear Regression for the Systems Shown in Figure 1**

| | $\Delta_{fus}H_{i,calc}$/J mol$^{-1}$ | $\Delta_{fus}H_{i,exp}{}^{a}$/J mol$^{-1}$ | dev. $\Delta_{fus}H_i$/% | $T_{fus,i,cal}$/K | $T_{fus,i,exp}{}^{a}$/K | dev. $T_{fus,i}$/% |
|---|---|---|---|---|---|---|
| cyclohexane | 3 085 | 2 760 | +11.8 | 280.1 | 279.8 | +0.1 |
| *p*-dichlorobenzene | 17 449 | 17 153 | +1.7 | 324.7 | 325.9 | −0.4 |
| indane | 7 880 | 8 598 | −8.4 | 220.6 | 221.0 | −0.2 |
| nitrobenzene | 10 349 | 11 590 | −10.7 | 280.0 | 278.9 | +0.4 |
| 3-heptanone | 17 333 | 17 532 | −1.1 | 236.1 | 236.0 | 0.0 |
| benzene | 9 650 | 9 789 | −1.4 | 279.3 | 278.7 | +0.2 |
| *p*-xylene | 16 907 | 16 805 | +0.6 | 286.6 | 286.4 | +0.1 |
| nitrobenzene | 11 555 | 11 590 | −0.3 | 279.0 | 278.9 | +0.1 |

[a] The experimental data were taken from the Dortmund Data Bank (DDB).

Figure 1 shows the graphical results for four binary systems. Table 1 contains the numerical results of the regressions in comparison with experimental calorimetric results for the enthalpies of fusion and melting temperatures as well as the deviations between experimental and predicted values. The results show a satisfactory agreement between experiment and prediction, particularly concerning the melting temperatures.

It is worthwhile to mention that the results we obtained were only received from one single SLE data set and not as a result of an evaluation of several measurements. Therefore, different results (e.g. for nitrobenzene) were obtained.

The deviations of the enthalpies of fusion for most compounds are smaller than ±3%; the deviations for melting temperatures are within ±0.4% (or ±1.2 K). The larger deviations for the enthalpies of fusion, e.g., for cyclohexane and indane are caused by different reasons: On one hand, the temperature range, from which the results for indane and cyclohexane are obtained, is rather small. Small deviations in the chosen plot can lead to large deviations in the results for the slope and axis intercept of eq 4. On the other hand, a correct prediction of the real phase behavior is necessary. Concerning the system indane + nitrobenzene (Jakob et al., 1995), the agreement between experimental SLE data and data predicted with modified UNIFAC (Dortmund) is not as good as for the other systems.

Further investigations show that the quality of the results mainly depends on the quality of the calculation of $\gamma_i^L$. First, the experimental solid−liquid equilibrium data of the system 2-heptanone + cyclohexane (Fiege, 1996)

**Table 2. Results of the Calculations for the System 2-Heptanone + Cyclohexane**

| | $\Delta_{fus}H_{i,calc}$/J mol$^{-1}$ | $\Delta_{fus}H_{i,exp}{}^{a}$/J mol$^{-1}$ | dev. $\Delta_{fus}H_i$/% | $T_{fus,i,cal}$/K | $T_{fus,i,exp}{}^{a}$/K | dev. $T_{fus,i}$/% |
|---|---|---|---|---|---|---|
| (a) Using ModifiedUNIFAC (Dortmund) To Predict the Real Behavior in the Liquid Phase | | | | | | |
| 2-heptanone | 19706 | 19712 | 0.0 | 238.4 | 238.4 | 0.0 |
| cyclohexane | 2010 | 2760 | −27.2 | 286.5 | 279.8 | +2.4 |
| (b) Under the Assumption of Ideal Behavior in the Liquid Phase | | | | | | |
| 2-heptanone | 31659 | 19712 | +60.6 | 237.3 | 238.4 | −0.5 |
| cyclohexane | 6619 | 2760 | +139.8 | 271.6 | 279.8 | −2.9 |

[a] The experimental data were taken from the Dortmund Data Bank (DDB).

**Table 3. Estimated Pure Component Properties Using Linear Regression for the Systems Shown in Figure 2**

| | $\Delta_{fus}H_{i,calc}$/J mol$^{-1}$ | $\Delta_{fus}H_{i,exp}{}^{a}$/J mol$^{-1}$ | dev. $\Delta_{fus}H_i$/% | $T_{fus,i,cal}$/K | $T_{fus,i,exp}{}^{a}$/K | dev. $T_{fus,i}$/% |
|---|---|---|---|---|---|---|
| cyclododecanol | 21 673 | | | 350.3 | 353.2 | −0.8 |
| tetracosane | 41 216 | 54 897 | −24.9 | 323.9 | 323.8 | 0.0 |
| cyclododecanol | 19 617 | | | 351.4 | 353.2 | −0.5 |
| octacosane | 60 477 | 64 648 | −6.5 | 334.8 | 334.7 | 0.0 |
| cyclododecanone | 17 317 | | | 333.8 | 334.2 | −0.1 |
| tetracosane | 61 729 | 54 897 | +12.5 | 323.1 | 323.8 | −0.2 |
| cyclododecanone | 16 201 | | | 334.1 | 335.2 | 0.0 |
| octacosane | 80 831 | 64 648 | +25.0 | 334.4 | 334.7 | −0.1 |

[a] The experimental data were taken from the Dortmund Data Bank (DDB).

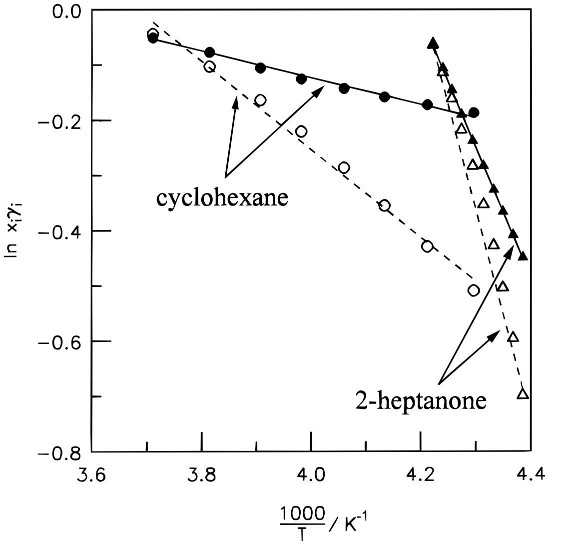

**Figure 2.** Plot for the system 2-heptanone + cyclohexane: (—) mod. UNIFAC (Do); (- - -) ideal behavior assumed.

were used for the estimation of the compounds' properties by applying modified UNIFAC (Dortmund). The results obtained, which are satisfying, except for the enthalpy of fusion of cyclohexane, are given in Table 2a. In the next step, the experimental data of the system 2-heptanone + cyclohexane were taken again and ideal behavior ($\gamma_i^L = 1$) was assumed. The results obtained are given in Table 2b; Figure 2 shows the corresponding plot. The dashed lines were obtained by linear regression from the nonfilled symbols representing the calculations on the basis of ideal behavior. The solid lines and the filled symbols show the results using modified UNIFAC (Dortmund). Obviously, neglection of the real behavior greatly influences the quality of the results. Since the "true" activity coefficients are greater than unity (positive deviation from Raoult's law), the estimated results for the enthalpies of fusion assuming ideal behavior are too large.

In the chosen plot the arrangement of the data points can be a criterion for the quality of the results. The more linear the course of the data points, the better the chosen model predicts the behavior of the real phase. The linearity and the good agreement between predicted and experimental results using modified UNIFAC (Dortmund) shows that this group contribution method is a very suitable tool for predictions of solid−liquid equilibria. This confirms the former investigations (Joh et al., 1997).

For the reasons mentioned above, the following conditions must be fulfilled in order to get good results:

(1) a sufficient amount of experimental SLE ($x_i^L$−T) data on both sides of the eutectic point

(2) a sufficient temperature range for a reliable evaluation

(3) a reliable description of the real behavior of the liquid phase

After the procedure was tested for systems with known pure component properties, systems with compounds (cyclododecanol, cyclododecanone) of unknown enthalpies of fusion and melting temperatures were considered. Figure 3 shows the graphical results; the corresponding values are given in Table 3. Using the procedure described above, the estimated enthalpies of fusion are approximately 16 500 J·mol$^{-1}$ for cyclododecanone and 20 500 J·mol$^{-1}$ for cyclododecanol.

***II. Estimation of the Molar Enthalpy of Transition $\Delta_{trs}H_i$ and the Transition Temperature $T_{trs,i}$.*** The plot of ln $x_i^L\gamma_i^L$ against 1/*T* considering eq 1 also allows calculation of the molar enthalpy of transition as well as transition temperatures of polymorphic species. This shall be explained for systems containing tetrachloromethane, which shows solid−solid transition at 225.35 K.

Besides experimental SLE data from the DDB, additional data were measured by the visual technique (Jakob et al., 1995), which is a fast and reliable method for the measurement of solid−liquid equilibria. The chemicals used for the determination of the system tetrachloromethane + *m*-xylene were obtained from Aldrich and distilled under reduced pressure using a Vigreux column (1.5 m in length). The resulting purities as well as the pure component properties are shown in Table 4. Figure 4 shows the obtained results in graphical form, and Table 5 gives the corresponding numerical SLE data.

For the intended calculations below the transition temperature, eq 1 has to be transformed:

$$\ln x_i^L\,\gamma_i^L = \left(-\frac{\Delta_{fus}H_i}{R} - \frac{\Delta_{trs}H_i}{R}\right)\cdot\frac{1}{T} + \left(\frac{\Delta_{fus}H_i}{RT_{fus,i}} + \frac{\Delta_{trs}H_i}{RT_{trs,i}}\right) \quad (5)$$

The slope of eq 5 contains the molar enthalpies of fusion and transition. In the axis intercept the molar enthalpies

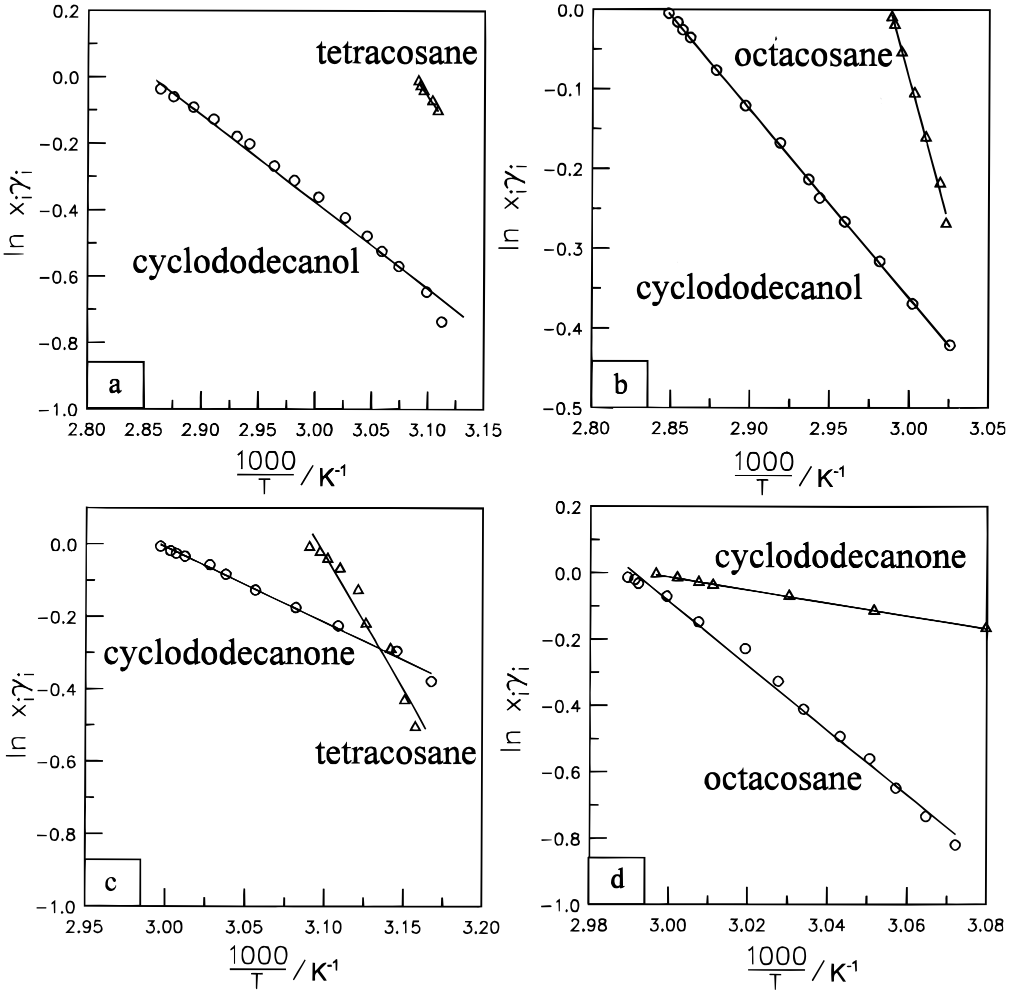

**Figure 3.** Plots for systems containing components with unknown enthalpy of fusion and melting temperature: (a) cyclododecanol + tetracosane (Lobbia et al., 1984); (b) cyclododecanol + octacosane (Lobbia et al., 1984); (c) cyclododecanone + tetracosane (Lobbia et al., 1981); (d) cyclododecanone + octacosane (Lobbia et al., 1981).

**Table 4. Purities and Pure Component Properties of the Applied Chemicals (Source: Dortmund Data Bank [DDB])**

| compound | CAS number | purity/% | $\Delta_{fus}H_i$/J mol$^{-1}$ | $T_{fus,i}$/K | $\Delta_{trs}H_i$/J mol$^{-1}$ | $T_{trs,i}$/K |
|---|---|---|---|---|---|---|
| tetrachloromethane | [56-23-5] | 99.99 | 2530 | 250.8 | 4560 | 225.4 |
| *m*-xylene | [108-38-3] | 99.96 | 11554 | 225.4 | | |

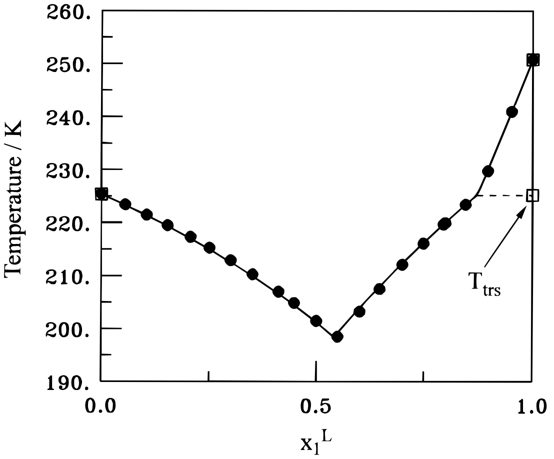

**Figure 4.** Solid−liquid equilibrium for the system tetrachloromethane (1) + *m*-xylene (2): (●) experimental data; (—) mod. UNIFAC (Do); (■) melting points of the pure components.

of fusion and transition as well as the corresponding temperatures are included. The desired properties can be estimated as follows:

**Table 5. Experimental SLE Data for the System Tetrachloromethane (1) + *m*-Xylene (2)**

| $x_1^L$ | *T*/K | $x_1^L$ | *T*/K | $x_1^L$ | *T*/K |
|---|---|---|---|---|---|
| 0.0000 | 225.44 | 0.4121 | 207.00 | 0.7953 | 219.70 |
| 0.0550 | 223.42 | 0.4482 | 204.87 | 0.7995 | 219.96 |
| 0.1047 | 221.49 | 0.5002 | 201.48 | 0.8461 | 223.44 |
| 0.1531 | 219.49 | 0.5497 | 198.50 | 0.8973 | 229.76 |
| 0.2064 | 217.29 | 0.6010 | 203.23 | 0.9517 | 240.97 |
| 0.2508 | 215.26 | 0.6475 | 207.50 | 1.0000 | 250.80 |
| 0.3003 | 212.92 | 0.7003 | 212.10 | | |
| 0.3514 | 210.27 | 0.7493 | 216.09 | | |

Using the experimental SLE data above the transition temperature and with the help of eq 4, the enthalpy of fusion $\Delta_{fus}H_i$ and the melting temperature $T_{fus,i}$ can be obtained. With these values and a regression of the data points below the transition temperature using eq 5, the values of the transition enthalpy $\Delta_{trs}H_i$ and the transition temperature $T_{trs,i}$ can be estimated. Figure 5 shows the corresponding plot, which contains a point of intersection of two straight lines representing the two polymorphic forms of tetrachloromethane. Table 6 contains the results of the calculation for tetrachloromethane. Satisfactory agreement is achieved between the results received from

**Table 6. Comparison between Experimental and Calculated Pure Component Properties for Tetrachloromethane**

| source of data | $\Delta_{fus}H$/ J mol$^{-1}$ | dev. $\Delta_{fus}H$/ % | $T_{fus}$/ K | dev. $T_{fus}$/ % | $\Delta_{trs}H$/ J mol$^{-1}$ | dev. $\Delta_{trs}H$/ % | $T_{trs}$/ K | dev. $T_{trs}$/ % |
|---|---|---|---|---|---|---|---|---|
| experimental calorimetric data, taken from DDB | 2530 | | 250.8 | | 4560 | | 225.4 | |
| *m*-xylene + $CCl_4$ (this work) | 2452 | −3.1 | 251.2 | +0.2 | 4372 | −4.1 | 225.8 | +0.2 |
| heptane + $CCl_4$ (Dahmani et al., 1988) | 2563 | +1.3 | 250.5 | −0.1 | 4067 | −10.8 | 224.2 | −0.5 |
| octane + $CCl_4$ (Dahmani et al., 1988) | 2535 | +0.2 | 250.7 | 0.0 | 4210 | −7.7 | 225.5 | 0.0 |
| octane + $CCl_4$ (Ott and Goates, 1983) | 2526 | −0.2 | 250.0 | −0.3 | 4377 | −4.0 | 225.0 | −0.2 |
| average | 2519 | −0.4 | 250.6 | −0.1 | 4257 | −6.6 | 225.1 | −0.1 |

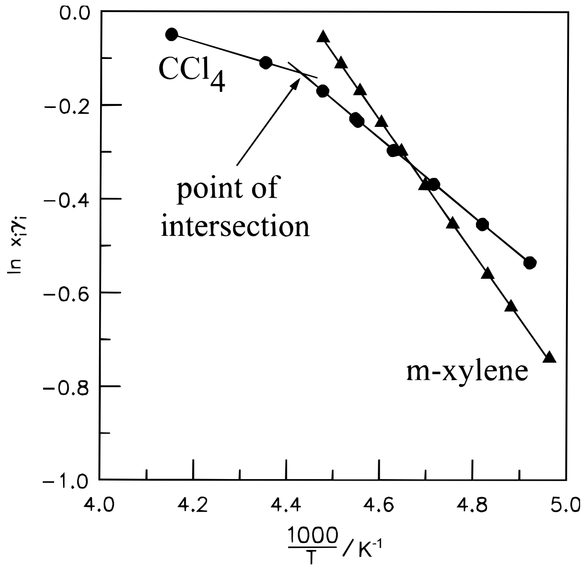

**Figure 5.** Plot of the system tetrachloromethane + *m*-xylene used for the estimation of the molar enthalpy of transition and transition temperature of tetrachloromethane.

the regressions of eqs 4 and 5, respectively, and the experimental data. The maximum deviations for the enthalpies of fusion are approximately 3% and for the enthalpies of transition approximately 11%. The corresponding temperatures ($T_{fus,i}$ and $T_{trs,i}$) can even be estimated within 0.5% (or ±1.2 K).

## Summary

In this paper a procedure for the estimation of pure component properties ($\Delta_{fus}H_i$, $T_{fus,i}$, $\Delta_{trs}H_i$, and $T_{trs,i}$) from experimental binary solid−liquid equilibrium data of eutectic systems is introduced. Using this procedure, good agreement between experimental and predicted values, especially for the melting temperatures and transition temperatures, is obtained. The basis for the correlations is a sufficient number of reliable experimental data as well as a good model for the description of the required activity coefficients in the temperature range covered. The calculations show that modified UNIFAC (Dortmund) is a suitable tool for the prediction of real phase behavior also at low temperatures.

To extend the database for systems containing tetrachloromethane, experimental solid−liquid equilibrium data of the system tetrachloromethane + *m*-xylene were measured.

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