# Excess Properties of the Mixture Bis(2-dichloroethyl)ether (Chlorex) + 2,2,4-Trimethylpentane (Isooctane)**

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The excess properties of the mixture bis(2-dichloroethyl)ether (chlorex) + 2,2,4-trimethylpentane (isooctane), i.e. excess volume $v^E$, excess enthalpy $h^E$, excess *Gibbs* energy $g^E$ and excess heat capacity $c_p^E$ are reported. The excess volume is small, negative on the chlorex side and positive on the isooctane side. The excess enthalpy at 293.15 K is 1 913 J mol$^{-1}$ for equimolar composition, the excess *Gibbs* energy amounts to 1 367 J mol$^{-1}$ under the same conditions. The system undergoes phase separation below 290.47 K. Due to the nearness of the critical point, $c_p^E$ exhibits a strong maximum at the critical composition ($x_{\text{isooctane}} = 0.508$), though the basic part of $c_p^E$ is negative. Discussion focusses on the effects of polarity of chlorex as mixing partner, on near-critical properties, and on mixing rules of a *van der Waals*-type equation of state.

*(Keywords: Excess properties of mixtures; Mixtures of polar + non-polar components; Critical properties; Equation of state for mixtures)*

*Exzeß-Eigenschaften der Mischungen Bis(2-dichlorethyl)ether (Chlorex) + 2,2,4-Trimethylpentan (Isooktan)*

Die Exzeßeigenschaften der Mischung Bis(2-dichlorethyl)ether (Chlorex) + 2,2,4-Trimethylpentan (Isooktan), d. s. Exzeßvolumen $v^E$, Exzeßenthalpie $h^E$, Exzeß-*Gibbs*-Energie $g^E$ und Exzeß-Wärmekapazität $c_p^E$ werden berichtet. Das Exzeßvolumen ist klein, negativ auf der Chlorex-Seite und positiv auf der Isooktan-Seite. Die Exzeßenthalpie beträgt für 293.15 K und äquimolare Zusammensetzung 1 913 J mol$^{-1}$, die Exzeß-*Gibbs*-Energie 1 367 J mol$^{-1}$ unter den gleichen Bedingungen. Das Mischsystem zeigt eine Phasentrennung unterhalb von 290.47 K. Wegen der Nähe des kritischen Punktes hat die Exzeß-Wärmekapazität $c_p^E$ ein starkes Maximum bei der kritischen Zusammensetzung ($x_{\text{isooctane}} = 0.508$), obwohl der Basis-Anteil von $c_p^E$ negativ ist. Die Diskussion behandelt die Effekte der Polarität von Chlorex als Mischungspartner, die Eigenschaften infolge der Nähe des kritischen Punktes und Mischungsregeln einer Zustandsgleichung vom *Van-der-Waals*-Typ.

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** Dedicated to Prof. Dr. *K. Komarek* on the occasion of his 60th birthday.

## Introduction

Recently [1], we have dealt with some aspects of a systematic study of excess properties of the same non-polar component, 2,2,4-trimethylpentane (isooctane), with polar components of different polarity, but without hydrogen bonds. Here we present the detailed results of the experimental investigation of the mixture isooctane + bis(2-dichloroethyl)ether (chlorex). A preliminary investigation of this was performed as early as 1949 by *Tschamler* et al. [2]. A special feature of this system is an upper critical point just below room temperature.

## Experimental

Isooctane (Res. grade, Phillips, U.S.A.) was fractionally distilled and stored in dark in vapour phase contact with a molecular sieve. Purity by g.l.c. was 99.98%. Chlorex (Puriss, Fluka, Federal Republic of Germany) was fractionally distilled under reduced pressure and otherwise treated in the same way. Purity as evidenced by g.l.c. was 99.41%. Densities, molar volumes, and heat capacities are given in Table 1, where

Table 1. *Densities* $(\rho)$, *molar volumes* $(v)$ *and heat capacities* $(c_p)$ *of the pure components*

| Substance | $T/K$ | $\rho/\mathrm{g\,cm^{-3}}$ | $v/\mathrm{cm^3\,mol^{-1}}$ | $c_p/\mathrm{JK^{-1}\,mol^{-1}}$ | $(c_p/v)/\mathrm{JK^{-1}\,cm^{-3}}$ |
|---|---|---|---|---|---|
| isooctane | 293.15 | 0.69192<br>0.69193[22] | 165.091 | 237.85 | 1.4435 |
|  | 298.15 | 0.68773<br>0.68781[22] | 166.097 | 238.50[22] |  |
|  | 313.15 | 0.67543 | 169.122 | 252.48 | 1.4925 |
| chlorex | 293.15 | 1.21626<br>1.2192[22]<br>1.2198[a] | 117.585 | 207.81 | 1.7673 |
|  | 298.15 | 1.21018 | 118.176 |  |  |
|  | 303.15 |  |  | 220.92[22] |  |
|  | 313.15 | 1.19249 | 119.929 | 211.93 | 1.7671 |
| benzene | 293.15 |  |  | 134.61 | 1.5147 |
|  | 313.15 |  |  | 138.69 | 1.5259 |
| cyclohexane | 293.15 |  |  | 155.13 | 1.4350 |
|  | 313.15 |  |  | 164.19 | 1.4816 |
| *n*-heptane | 293.15 |  |  | 222.88 | 1.5209 |
|  | 313.15 |  |  | 230.52 | 1.5333 |

[a] This density given by Ref. [2] refers to water at 293.15 K. Probably the density given by Ref. [22] has also to be corrected by the density ratio of water between 293.15 K and 277.15 K.

Table 2. *Density and excess volume of chlorex + isooctane (2) at 293.15 K. The column $\Delta v^E$ gives the difference between experiment and the Redlich-Kister correlation of Table 5*

| $x_2$ | $\rho/\mathrm{g\,cm}^{-3}$ | $v^E/\mathrm{cm}^3\mathrm{mol}^{-1}$ | $\Delta v^E/\mathrm{cm}^3\mathrm{mol}^{-1}$ |
|---|---|---|---|
| 0.00000 | 1.21640 | 0.000 | 0.000 |
| 0.02967 | 1.19515 | − 0.034 | 0.001 |
| 0.04682 | 1.18307 | − 0.052 | − 0.001 |
| 0.09479 | 1.14985 | − 0.074 | 0.003 |
| 0.20026 | 1.08060 | − 0.077 | 0.002 |
| 0.27527 | 1.03441 | − 0.058 | − 0.001 |
| 0.30767 | 1.01524 | − 0.052 | − 0.007 |
| 0.39747 | 0.96423 | − 0.009 | 0.000 |
| 0.44262 | 0.93982 | 0.006 | − 0.005 |
| 0.46225 | 0.92934 | 0.028 | 0.008 |
| 0.54622 | 0.88646 | 0.062 | 0.003 |
| 0.55996 | 0.87964 | 0.072 | 0.006 |
| 0.69048 | 0.81811 | 0.127 | − 0.005 |
| 0.70728 | 0.81054 | 0:137 | − 0.003 |
| 0.77759 | 0.77981 | 0.165 | − 0.001 |
| 0.80022 | 0.77019 | 0.176 | 0.005 |
| 0.87718 | 0.73866 | 0.167 | 0.005 |
| 0.93495 | 0.71612 | 0.117 | 0.001 |
| 0.96964 | 0.70304 | 0.064 | − 0.001 |
| 1.00000 | 0.69188 | 0.000 | 0.000 |

Table 3. *The same as Table 2, but at 298.15 K*

| $x_2$ | $\rho/\mathrm{g\,cm}^{-3}$ | $v^E/\mathrm{cm}^3\mathrm{mol}^{-1}$ | $\Delta v^E/\mathrm{cm}^{-3}\mathrm{mol}^{-1}$ |
|---|---|---|---|
| 0.00000 | 1.21048 | 0.000 | 0.000 |
| 0.35796 | 0.98106 | − 0.038 | 0.002 |
| 0.44248 | 0.93483 | − 0.004 | − 0.004 |
| 0.59001 | 0.86015 | 0.085 | 0.001 |
| 0.64051 | 0.83625 | 0.113 | − 0.001 |
| 0.78934 | 0.77029 | 0.171 | − 0.009 |
| 1.00000 | 0.68773 | 0.000 | 0.000 |

also literature values are quoted. Excess volumes were calculated from densities, which were determined by a vibrating tube densimeter (A. Paar, Austria) [3, 4]; mixtures were prepared from degassed samples. Excess enthalpies were determined [4, 5] with a flow calorimeter of the Picker design (Setaram, France) in the discontinuous mode, where the flow rate was controlled volumetrically and the mixture composition was controlled by passing the mixture through a vibrating tube densimeter. The excess heat capacity was calculated from differences in heat

Table 4. *The same as Table 2, but at 313.15 K*

| $x_2$ | $\rho/\text{g cm}^{-3}$ | $v^E/\text{cm}^3\,\text{mol}^{-1}$ | $\Delta v^E/\text{cm}^3\,\text{mol}^{-1}$ |
|---|---|---|---|
| 0.00000 | 1.19249 | 0.000 | 0.000 |
| 0.04682 | 1.15934 | − 0.038 | 0.001 |
| 0.17912 | 1.07173 | − 0.111 | − 0.004 |
| 0.18927 | 1.06535 | − 0.115 | − 0.005 |
| 0.27527 | 1.01290 | − 0.105 | 0.007 |
| 0.31041 | 0.99241 | − 0.099 | 0.005 |
| 0.39747 | 0.94368 | − 0.063 | 0.001 |
| 0.46225 | 0.90925 | − 0.022 | − 0.003 |
| 0.54582 | 0.86700 | 0.044 | − 0.009 |
| 0.62072 | 0.83104 | 0.117 | − 0.002 |
| 0.72876 | 0.78229 | 0.210 | 0.014 |
| 0.80022 | 0.75212 | 0.216 | − 0.000 |
| 0.89525 | 0.71423 | 0.173 | − 0.003 |
| 0.92762 | 0.70191 | 0.135 | − 0.004 |
| 1.00000 | 0.67537 | 0.000 | 0.000 |

Table 5. *The Redlich-Kister correlation for $v^E$ with an assumed linear temperature dependence $[A_i/\text{cm}^3\,\text{mol}^{-1} = a_i + b_i\,(T - 300.15)]$ and for $h^E/J\,\text{mol}^{-1}$ at 298.15 K*

| | | $i = 0$ | $i = 1$ | $i = 2$ | $i = 3$ |
|---|---|---|---|---|---|
| $v^E$: | $a_i$ | 0.11384 | 1.2083 | 0.51691 | 0.64834 |
| | $b_i$ | − 0.00499 | 0.0384 | 0.01937 | − 0.05021 |
| $h^E$: | $A_i$ | 7 792.4 | − 779.3 | 797.3 | |

capacities per unit volume, determined with a differential flow calorimeter (Setaram, France) [4, 6, 7] between samples of not too different volumetric heat capacities. Excess *Gibbs* energies were calculated from the coexistence curve between the critical point (290.47 K) and 282.26 K, where the phase separation covers already about two thirds of the concentration interval. The coexistence curve was determined [4] by visual observation of stirred mixtures, which were cooled very slowly (less than 1 mK s$^{-1}$) in a isolated bottle, where a Pt resistance thermometer was immersed.

## Results

*Excess Volumes.* Results (at temperatures: 293.15 K, 298.15 K and 313.15 K) are presented in Table 2–4 (direct experimental values), and in form of a *Redlich-Kister* correlation

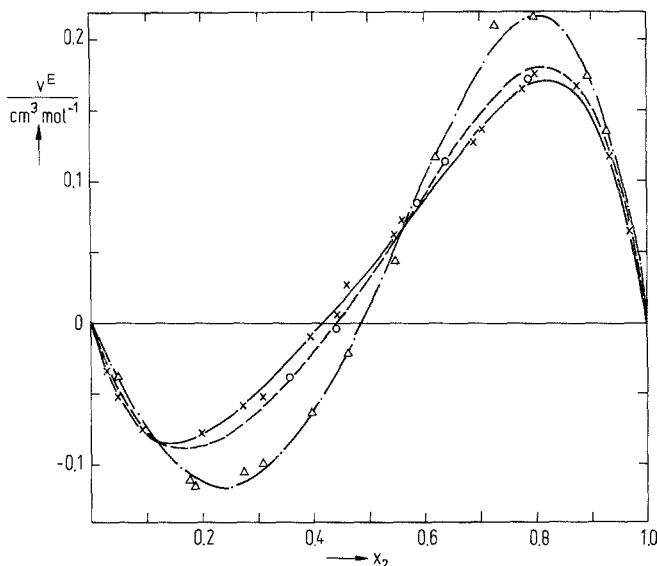$$v^E = x_2(1 - x_2) \sum A_i(2 x_2 - 1)^i \tag{1}$$

Fig. 1. The excess volume $v^E$ of chlorex + isooctane (2) at 293.15 K (crosses, full line), 298.15 K (circles, dotted line), and 313.15 K (triangles, dash-dotted line). The curves correspond to the *Redlich-Kister* correlation with an assumed linear temperature dependence

in Table 5 ($x_2$ ... mole fraction of isooctane); they are also shown in Fig. 1, where the full curves are the *Redlich-Kister* correlations. It is seen that the main temperature effect on the sigmoid curve is a flattening around the critical composition ($x_2 = 0.508$), which will be discussed below.

*Excess Enthalpies.* These are given in Table 6 and Fig. 2. The *Redlich-Kister* correlation is included in Table 5. The temperature of the experiment was set to 298.15 K in order to avoid difficulties from the nearness of phase separation.

*Excess Heat Capacities.* Differences in volumetric heat capacities were determined between heptane (used as reference substance) and benzene, benzene and isooctane, isooctane and cyclohexane, and from isooctane to chlorex between each mixture. The results for the volumetric heat capacities of the pure components are included in Table 1, the results for the excess quantities are presented in Table 7 and 8 and Fig. 3, the *Redlich-Kister* correlations are included in the Tables. The $c_p^E$-curve is very much affected by the nearness of the critical point, which will be discussed below. For these discussions it is an unfortunate circumstance, that the method of measurement does not permit the instalment of an exact

Table 6. *Excess enthalpies of chlorex* + *isooctane (2) at 298.15 K.* $\Delta h^E$ *denotes the difference between experiment and Redlich-Kister correlation of Table 5*

| $x_2$ | $\dfrac{h^E}{\text{J mol}^{-1}}$ | $\dfrac{\Delta h^E}{\text{J mol}^{-1}}$ | $\dfrac{h^E/(x_1 \cdot x_2)}{\text{J mol}^{-1}}$ | $\dfrac{\Delta h^E/(x_1 \cdot x_2)}{\text{J mol}^{-1}}$ |
|---|---|---|---|---|
| 0.0000 | 0.0 | 0.0 | — | — |
| 0.1202 | 955.2 | 19.8 | 9 031.0 | 186.8 |
| 0.1830 | 1 286.7 | 0.1 | 8 607.6 | 0.6 |
| 0.2287 | 1 479.6 | − 10.8 | 8 389.1 | − 61.0 |
| 0.2679 | 1 629.7 | − 3.1 | 8 310.0 | − 16.0 |
| 0.2968 | 1 715.8 | − 4.2 | 8 220.7 | − 20.0 |
| 0.3149 | 1 761.7 | − 5.2 | 8 165.9 | − 24.1 |
| 0.3486 | 1 843.0 | 3.4 | 8 116.5 | 15.0 |
| 0.3826 | 1 896.8 | 2.5 | 8 029.9 | 10.7 |
| 0.4056 | 1 918.9 | − 2.1 | 7 959.1 | − 8.7 |
| 0.4356 | 1 941.5 | − 2.3 | 7 896.7 | − 9.2 |
| 0.4651 | 1 951.9 | − 1.2 | 7 845.6 | − 5.0 |
| 0.5131 | 1 948.1 | 6.3 | 7 797.8 | 25.3 |
| 0.5726 | 1 888.5 | 5.1 | 7 716.7 | 20.7 |
| 0.6685 | 1 701.9 | 13.1 | 7 679.5 | 59.2 |
| 0.7301 | 1 483.2 | − 14.8 | 7 527.6 | − 75.0 |
| 0.7919 | 1 248.3 | − 5.4 | 7 576.1 | − 33.1 |
| 0.8721 | 857.8 | 4.4 | 7 693.1 | 39.0 |
| 1.0000 | 0.0 | 0.0 | — | — |
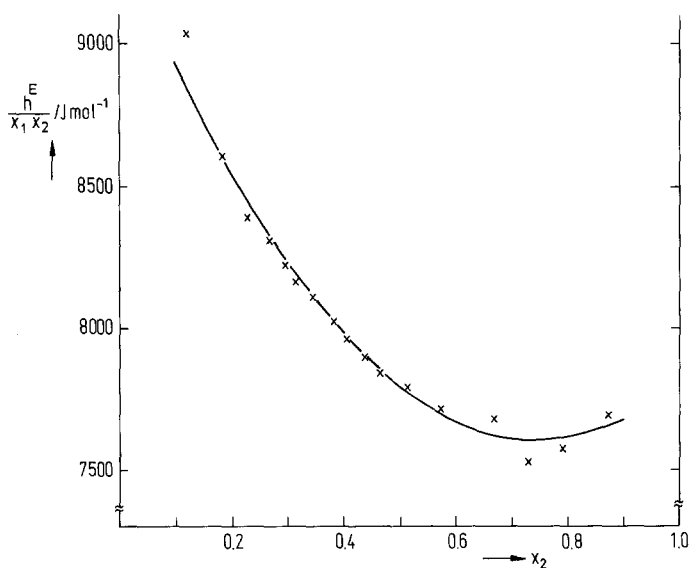


Fig. 2. The excess enthalpy $h^E$ of chlorex + isooctane (2) at 298.15 K, reduced by the product of molefractions. Crosses are experimental, the curve is the *Redlich-Kister* correlation

Table 7. *The excess heat capacities of chlorex + isooctane (2) at 293.15 K. $\Delta c_p^E$ gives the difference between experiment and four parameter Redlich-Kister correlation ($A_0 = 27.413$, $A_1 = -1.876$, $A_2 = -60.238$, $A_3 = -6.074$), $\delta c_p^E$ between experiment and three parameter Redlich-Kister correlation [$A_0 = 27.407$, $A_1 = -4.0273$, $A_2 = -60.067$, cf. the discussion leading to equ. (11)]*

| $x_2$ | $c_p^E$/J mol$^{-1}$ K$^{-1}$ | $\Delta c_p^E$/J mol$^{-1}$ K$^{-1}$ | $\delta c_p^E$/J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| 0.0000 | 0.000 | 0.000 | — |
| 0.0297 | − 0.449 | 0.100 | 0.183 |
| 0.0948 | − 0.643 | − 0.008 | 0.110 |
| 0.1966 | 1.167 | − 0.053 | − 0.055 |
| 0.3077 | 4.192 | 0.024 | − 0.084 |
| 0.4426 | 6.637 | 0.014 | − 0.043 |
| 0.5600 | 6.484 | 0.001 | 0.063 |
| 0.6905 | 3.740 | − 0.026 | 0.074 |
| 0.7776 | 1.197 | 0.027 | 0.046 |
| 0.8772 | − 1.208 | − 0.035 | − 0.151 |
| 0.9696 | − 0.892 | 0.065 | − 0.027 |
| 1.0000 | 0.000 | 0.000 | — |

Table 8. *The same as Table 7, but for 313.15 K. The Redlich-Kister parameters are $A_0 = 2.360$, $A_1 = -1.982$, $A_2 = -18.898$, $A_3 = 1.250$ and $A_0 = 2.3522$, $A_1 = -1.5386$, $A_2 = -18.863$, respectively*

| $x_2$ | $c_p^E$/J mol$^{-1}$ K$^{-1}$ | $\Delta c_p^E$/J mol$^{-1}$ K$^{-1}$ | $\delta c_p^E$/J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| 0.0000 | 0.000 | 0.000 | — |
| 0.0308 | − 0.373 | 0.029 | 0.010 |
| 0.0684 | − 0.722 | − 0.033 | − 0.061 |
| 0.1893 | − 0.594 | 0.020 | 0.016 |
| 0.3104 | 0.052 | − 0.018 | 0.004 |
| 0.4165 | 0.537 | 0.012 | 0.030 |
| 0.5458 | 0.506 | 0.005 | − 0.003 |
| 0.6207 | 0.173 | − 0.015 | − 0.034 |
| 0.7288 | − 0.475 | − 0.004 | − 0.020 |
| 0.8580 | − 0.972 | 0.038 | 0.054 |
| 0.9276 | − 0.871 | − 0.040 | − 0.014 |
| 1.0000 | 0.000 | 0.000 | — |

temperature $T$, but refers to a temperature interval between $T - 0.5$ and $T + 0.5$ K.

*Consolute Curve.* The experimentally determined points of the consolute curve are listed in Table 9. They are correlated by a cubic relation between $T_c - T$ and $|x - x_c|$; the corresponding graph gives $T_c = 290.47$ K and $x_{2,c}$ (2 = isooctane) = 0.508. Whereas the $(T_c - T)^{1/3}$
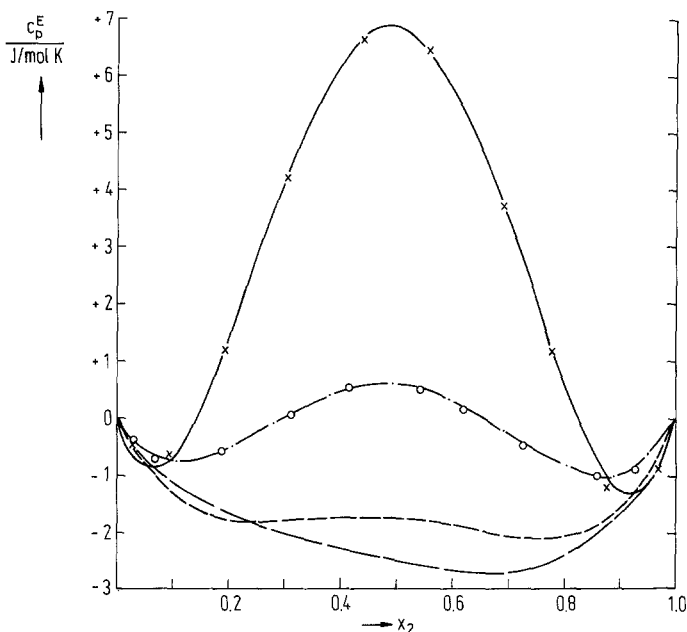
Fig. 3. The excess heat capacity $c_p^E$ of chlorex + isooctane (2) at 293.15 K (crosses: experimental, full curve: *Redlich-Kister* correlation, long-dashed curve: assumed basic part) and 313.15 K (circles: experimental, dash-dotted curve: *Redlich-Kister* correlation, short-dashed curve: assumed basic part)

vs. $x_2 - x_c$ relation is linear on the isooctane side over the whole temperature interval investigated, an additional term is needed on the chlorex side. The relations are quoted in Table 9 also. It is seen that the two phase region becomes a bit wider on the chlorex side a few degrees below $T_c$ and becomes almost symmetrical again at lower temperatures.

   *Excess Gibbs Energies.* Excess *Gibbs* energies were calculated numerically from the consolute curve by a method given before [8, 9]. The method involves extrapolation of $\partial g^E/\partial x$ over the composition region of the homogeneous mixture to $x = 0$ and $x = 1$, which involves an arbitrary element. The excess *Gibbs* energy obtained in this way and calculated for the critical temperature of 290.47 K was correlated by a three parameter *Redlich-Kister* equation, which was used in turn to verify the consolute curve. In this recalculation procedure, two coefficients are given by the condition of phase equilibrium, the third coefficient (in the present case $A_2$) has to be chosen arbitrarily, which corresponds to the arbitrariness of the extrapolation of $\partial g^E/\partial x$ to the edges of the composition interval. $A_2$ as given by this extrapolation was used and then calculated for lower

Table 9. *Measured values of the consolute curve of chlorex + isooctane (2) and their correlation with a cubic form*

| $x_2$ | $T/K$ | $(290.47 - T)/K$ | $(0.508 - x_2)^3 \cdot 261 \, [1 + (0.508 - x_2)^6 \, 510]$ |
|---|---|---|---|
| 0.2132 | 281.56 | 8.91 | 8,93 |
| 0.2364 | 284.02 | 6.45 | 6.30 |
| 0.2561 | 285.91 | 4.56 | 4.72 |
| 0.2706 | 286.60 | 3.87 | 3.81 |
| 0.2859 | 287.46 | 3.01 | 3.03 |
| 0.3080 | 288.54 | 1.93 | 2.16 |
| 0.3481 | 289.16 | 1.31 | 1.21 |
| 0.3715 | 289.78 | 0.69 | 0.67 |
| 0.4507 | 290.31 | 0.16 | 0.05 |
| 0.5185 | 290.47 | 0.00 | $(x_2 - 0.508)^3 \cdot 409.4$ |
| 0.5767 | 290.37 | 0.10 | 0.13 |
| 0.6052 | 289.97 | 0.50 | 0.38 |
| 0.6278 | 289.63 | 0.84 | 0.70 |
| 0.6478 | 289.36 | 1.11 | 1.12 |
| 0.6724 | 288.53 | 1.94 | 1.82 |
| 0.7208 | 286.63 | 3.84 | 3.95 |
| 0.7634 | 283.65 | 6.82 | 6.82 |
| 0.7820 | 282.05 | 8.42 | 8.42 |
| 0.8090 | 279.55 | 10.92 | 11.16 |

Table 10. *The excess properties $g^E$, $h^E$ and $s^E$ of chlorex + isooctane (2) at the critical solution temperature of 290.47 K*

$$g^E/J \, mol^{-1} = x_1 x_2 [5\,488.9 + 9.4(2\,x_2 - 1) + 659.0(2\,x_2 - 1)^2]$$
$$h^E/J \, mol^{-1} = x_1 x_2 [7\,575.0 - 749.5(2\,x_2 - 1) + 1\,279.5(2\,x_2 - 1)^2]$$
$$s^E/J \, K^{-1} mol^{-1} = x_1 x_2 [7.181 - 2.612(2\,x_2 - 1) + 2.136(2\,x_2 - 1)^2]$$

temperatures by means of the $s^E$-term and an extrapolation of the corresponding term in $c_p^E$ by assuming linear temperature dependence. Table 10 gives the *Redlich-Kister* relations for $g^E$, $h^E$, and $s^E$ at the critical temperature 290.47 K ($h^E$ obtained by integrating over $c_p^E$—correlated by extended scaling as discussed later—between 298.15 K and 290.47 K). Fig. 4 shows the coefficients of the *Redlich-Kister* correlation as function of temperature as given by the phase equilibrium. They are compared with the expected temperature variation given by $s^E$ and a linear temperature variation of $c_p^E$ (full lines in Fig. 4). It is seen that the detailed variation of the consolute curve, especially near the critical point, cannot be given by a three parameter *Redlich-Kister* equation, which is no surprise. But the coarse behaviour of the correlation is all right.
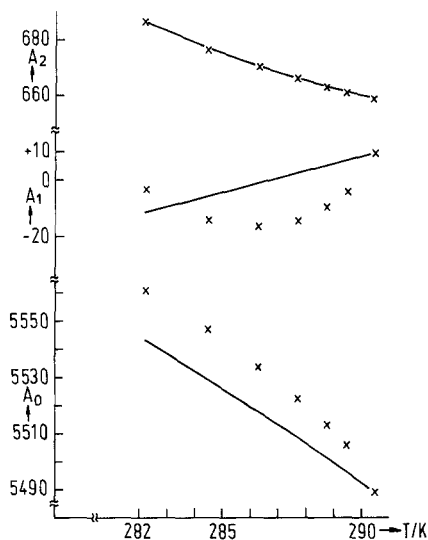
Fig. 4. The coefficients of the three-parameter *Redlich-Kister* representation of the excess *Gibbs* energy $g^E$ of chlorex + isooctane (cf. Table 10) as function of temperature. Full curves are calculated via $s^E_{290.47}$ and an assumed linear temperature dependence of $c^E_p$. Crosses are calculated from the consolute curve

## Discussion

The initial aim of the investigation was to determine excess properties of a system with a non-polar and a polar, but non-associated component. The nearness to the liquid-liquid critical point makes it possible to discuss also some facts typical for the critical region, though a detailed investigation of critical properties would require additional experiments at definite but small distances from the critical temperature. Finally the experimental results on the mixture are used for a check on the mixing rules for a recently proposed equation of state.

### *Polarity of Chlorex and the Temperature Dependence of the Excess Properties*

As discussed before [1], the polarity of chlorex should not be judged by its quite big absolute dipole moment ($\mu = 2.60$ D), but rather by its reduced moment $\mu^* = \sqrt{\mu^2/(\sigma^3 \varepsilon)}$ (with $\varepsilon$ the minimum and $\sigma$ the zero of its pair potential). An estimate of $\sigma$ and $\varepsilon$ along the line of an old cell model treatment [10] gave $\mu^* = 0.662$, which is a medium value. This is due to the relatively large size of the molecule, and its rather strong pair potential already indicated by the high boiling point.

For a not too strong dipole moment, the angle dependent dipole-dipole contribution to the pair potential can be averaged to give a spherically symmetrical but temperature dependent contribution proportional to $1/T$. For the pair potentials near their minimum, $u_{ij}$,

$$u_{11} = u_{11,\text{disp}} + u_{11,\text{ind}} - b_1/T$$
$$u_{12} = u_{12,\text{disp}} + u_{12,\text{ind}} \tag{2}$$
$$u_{22} = u_{22,\text{disp}}$$

where the subscript 1 refers to the polar chlorex molecule, the interchange energy

$$w = 2u_{12} - u_{11} = u_{22} \tag{3}$$

might be formulated by

$$w = a + b_1/T. \tag{4}$$

Here $a$ is the difference between the dispersion and induction contribution of the pair potential, which is independent of temperature for spherical molecules. For molecules of anisotropic shape, the angle-dependent part of this contribution might again be treated approximately as a spherical but temperature dependent term, being proportional to $1/T$, thus

$$a = A + b_2/T. \tag{5}$$

Summing up the terms $b_1 + b_2 = B$, the final result is

$$w = A + B/T. \tag{6}$$

As in a primitive mixture model [11] $g^E$ is proportional to $w$, $h^E$ turns out to be proportional to $A + 2B/T$, and

$$c_p^E = -2(h^E - g^E)/T. \tag{7}$$

When $B$ is only given by $b_2$, that is in absence of any polarity of the molecules, this relation seems to be fulfilled indeed [12]. But for mixtures of polar + non-polar components, $c_p^E$ is usually more positive than demanded by equ. (7), which indicates that some dipole-dipole orientations have a stronger preference (one may think in the direction of the weak association) than accounted for by the angle-averaging procedure leading to equ. (2) and (4). In the case of the present mixture, this additional contribution is rather difficult to judge, because $c_p^E$ contains a big contribution due to the near-critical behaviour, and the basic part is somewhat uncertain. Using the correlation for the anomalous part as discussed later, the basic value of $c_p^E$ at equimolar composition would be $-2.5\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$ at 293.15 K and $-1.75\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$ at 313.15 K, whereas equ. (7) would result in $-3.72\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$ at 293.15 K and $-4.19\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$ at 313.15 K. Since a near-critical part in $h^E$ was not

subtracted, this comparison has more validity at 313.15 K. Anyhow, $c_p^E$ as given by equ. (7) is again more negative than the experimental value, but the difference is not dramatic, as to be expected for a polar component with medium polarity.

### Properties Due to the Critical Region

On approaching the critical point from the homogeneous region, the curves for $h^E$ and $v^E$ should flatten [12], and, in general, this flattening is connected with a temperature derivative along $x_c$ with tends to infinity at $T_c$. In the present case, this is obeyed by $c_p^E$, where this behaviour is emphasized by the large value of $h^E$, but it cannot be observed for $\partial v^E/\partial T$. The flattening of the $v^E$-curve is readily seen, but it is not connected with a large temperature derivative. This might have to do with two facts: (1) that the $v^E$-curve is sigmoid for this system, and (2) that $v^E$ is almost zero at $x_c$. When the $v^E$-curves at 293.15 K, 298.15 K and 313.15 K are fitted with a common *Redlich-Kister* correlation with coefficients linearly dependent on temperature, the 298.15 K-curve is perfectly correlated (cf. Fig. 1). If the temperature dependence deviates from the linear one between 293.15 K and 298.15 K this dependence is weaker than linear.

It should be emphasized that a *Redlich-Kister* correlation is insufficient to show the detailed concentration behaviour around the critical point, which is non-analytic [13]. This is the reason, that the *Redlich-Kister* correlation does not lead to $\partial^2 v^E/\partial x^2 = 0$ at $x = x_c$, for which it would be necessary that $A_0$ becomes equal to $A_2$ (as $x_c$ is almost 0.5). Though for $v^E$ $A_0$ increases and $A_2$ decreases in approaching the critical temperature, the fit with an assumed linear temperature dependence gives $A_0 = 0.1518$ and $A_2 = 0.3294$ at the critical temperature.

In the present system, the anomalous part of $c_p^E$ is quite impressive. This is because the basic part of $c_p^E$ is negative, so that the anomalous part can be much better seen than if it would be on top of a positive basic part. Inspite of the fact that the measurements are too scarce and too uncertain with respect to a definite temperature difference to the critical temperature, some kind of correlation will be tried on the anomalous part. This is also to show the possibilities of considering the composition variation. In other work [14, 15] aimed directly at determining the critical behaviour only the temperature variation at the critical composition has been investigated. First, according to these papers the anomalous part of $c_p^E$ at $x_c$ is correlated by extended scaling,

$$c_{p,\text{anomal}}^E = A\left[t^{-0.11}(1 + D\,t^{0.5}) - 1 - D\right], \qquad (8)$$

with

$$t = (T - T_c)/T_c. \qquad (9)$$

The determination of $A$ and $D$ involves an estimation of the basic part of $c_p^E$ and is to a certain degree arbitrary in view of only two values of $t$ (0.0029964 and 0.07808, resp.). Finally $D = 0.37$ was chosen consequently leading to $A = 25.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

The next step is to investigate the consequences for the composition behaviour. Starting from a temperature $T'$, where liquid-liquid phase separation is established, the composition is looked for, where $T'$ is the critical temperature in the sense that the anomalous part of $c_p^E$ tends there to infinity. Forming $t$ according to

$$t = (T - T')/T', \tag{10}$$

one can calculate $c_{p,\mathrm{anomal}}^E$ by equ. (8) and compare it with the composition dependence of the anomalous part. This way one obtains the mole fraction $x'$ for which $T'$ is the "critical" temperature. It will be shown that $x'$ is located between the consolute curve and the spinodal curve. For the composition dependence of the anomalous part the three parameter version of the *Redlich-Kister* correlation of $c_p^E$ of Tables 7 and 8 is considered, and $c_{p,\mathrm{anomal}}^E$ will be presented tentatively by

$$c_{p,\mathrm{anomal}}^E = x_1 x_2 \left[A_{0,\mathrm{anomal}} + A_{2,\mathrm{anomal}}(2x_2 - 1)^2\right]. \tag{11}$$

The coefficients $A_{0,\mathrm{anomal}}^{20}$ and $A_{0,\mathrm{anomal}}^{40}$—for 293.15 K and 313.15 K—are given by the choice of $A$ and $D$ of equ. (8). A slight correction for $A_{0,\mathrm{anomal}}^{20}$ is appropriate as $c_{p,\mathrm{anomal}}^E$ tends to develop a peak at $x_2 = x_c$ when approaching $T_c$. The coefficient $A_{2,\mathrm{anomal}}^{20}$ is chosen such that the remaining

Table 11. *The splitting of the Redlich-Kister representation of $c_p^E/J\,K^{-1}\,mol^{-1}$ into an anomalous part and a basic part (cf. Tables 7 and 8)*

| $T = 313.15\,\mathrm{K}$ | $A_0$ | $A_1$ | $A_2$ |
|---|---|---|---|
| total | 2.3522 | $-1.5386$ | $-18.863$ |
| anomalous part | 9.336 | 0.0 | $-4.0$ |
| basic part | $-6.984$ | $-1.5386$ | $-14.863$ |
| $T = 293.15\,\mathrm{K}$ | $A_0$ | $A_1$ | $A_2$ |
| total | 27.407 | $-4.03$ | $-60.067$ |
| anomalous part | 37.407[a] | 0.0 | $-52.0$ |
| basic part | $-10.0$ | $-4.03$ | $-8.067$ |

[a] For mole fractions $0.42 > x_2 > 0.58$ a value of 36.81 has been used to correct for the tendency of $c_p^E$ to develop a peak at $x_2 = 0.508$.
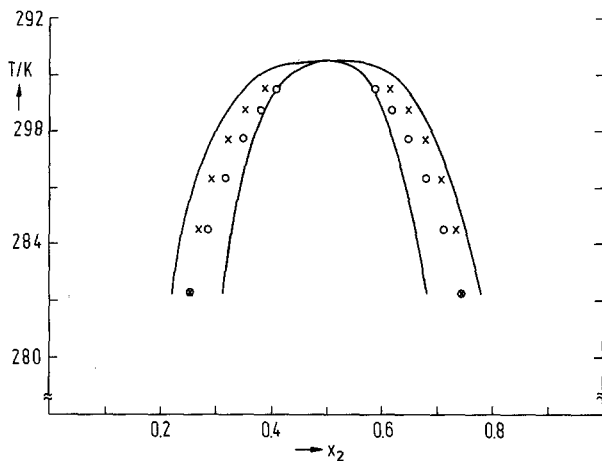
Fig. 5. The consolute curve and the spinodal curve (calculated via the *Redlich-Kister* expressions for $g^E$) of chlorex + isooctane (2). Crosses and circles indicate, where $c_p^E$ should bekome infinite according to extended scaling. Crosses are calculated from the 293.15 K values, circles from the 313.15 K values of $c_p^E$

$A_2$ for the basic part is not too negative. Consequently $A_{2,\text{anomal}}^{40}$ is determined in such a way that $x'$ is identical for the lowest temperature $T'$ = 282.26 K, whether determined by the $c_{p,\text{anomal}}^E$-curve at 293.15 K or at 313.15 K. The resulting division of the *Redlich-Kister* presentation of $c_p^E$ into an anomalous and a basic part is given in Table 11, with the basic part indicated in Fig. 3. The combination of equ. (11) with the extended scaling [equ. (8)] for compositions aside the critical one is shown in Fig. 5. The inadequacy of a *Redlich-Kister* correlation for the anomalous part reveals itself by the fact that the mole fractions $x'$ for a given $T'$ are somewhat different when determined from the 293.15 K or 313.15 K-curve. But the result seems to be valid that $x'$ is near the spinodal curve (determined by the *Redlich-Kister* correlation for $g^E$) when $T'$ is near $T_c$ and tends to move towards the coexistence curve when $T'$ goes away from $T_c$. The same result has been obtained for different choices of $D$, $A$, and $A_{2,\text{anomal}}$. It is in line with considerations on spinodal decomposition [16] for small molecules and relatively short ranged intermolecular forces.

## Calculation of $g^E$ and $h^E$ from Density Measurements

It has been shown [17] that for the mixture benzene + cyclohexane $g^E$ and $h^E$ could be calculated from density measurements, i.e. from $v^E$, by using the high density approximation of a *van der Waals*-type equation of state for anisotropic molecules. The problems involved for mixtures of

polar + non-polar components and possible ways of solution have been dealt with in a recent paper [18]. The theory will be briefly summarized and then applied for the chlorex + isooctane system.

The equation of state is written as

$$Z = Z_h - \frac{a_0}{v^*} \frac{y}{RT} + Z_{corr}, \tag{12}$$

where the compressibility factor $Z = pv/(RT)$ is divided into a hard part $Z_h$ arising form the repulsive forces and an attractive part $- (a_0/v^*)$ $(y/RT)$, assumed to be linear with reduced density $y = v^*/v$ at high densities. The proportionality constant for the attractive energy is denoted by $a_0/v^*$, with $v^*$ being the volume of one mole hard convex bodies. $Z_{corr}$ is a correction term to account for the non-linear density dependence of the attractive term at low and medium densities. The hard part $Z_h$ contains an antisphericity parameter which is derived from molecular models [19], and the parameter $v^*$. The parameters $v^*$ and $a_0/v^*$ are adjusted by using the experimental values of volume and isothermal compressibility on the liquid side of the orthobaric curve and assuming that the density is sufficiently high to justify $Z_{corr} = 0$.

The residual reduced *Helmholtz* energy $f^*/(RT)$ is obtained by integration of the equation of state from zero density to the density in question: thus

$$\frac{f^*}{RT} = \left( \frac{f^*}{RT} \right)_h - \frac{a_0}{v^*} \frac{y}{RT} + \int_0^y \frac{Z_{corr}}{y} \, dy. \tag{13}$$

When $y$ is sufficiently big so that there $Z_{corr} = 0$, the last term becomes a constant, called the *Helmholtz* energy integration constant

$$\frac{a'}{v^* RT} = \int_0^y \frac{Z_{corr}}{y} \, dy. \tag{14}$$

For a binary mixture at effectively zero pressure, it follows that

$$\frac{g^E}{RT} = \left[ \left( \frac{f^*}{RT} \right)_h - \frac{a_0}{v^*} \frac{y}{RT} + \frac{a'}{v^* RT} - \ln v \right]_{Mi} - x_1 [\ ]_1 - x_2 [\ ]_2. \tag{15}$$

The problem is then to calculate the terms for the mixture from pure component properties or additional measurements.

The properties of the hard convex body fluid are given by theory, so the first term can be calculated. When the volume of the mixture, i.e. $v^E$, is known, the parameter $(a_0/v^*)_{Mi}$ can be evaluated from the high density

equation of state at zero pressure, i.e. equ. (12) with $Z = 0$ and $Z_{corr} = 0$. Thus the only problem left is to determine $(a'/v^*)_{Mi}$. Our aim is to relate $(a'/v^*)_{Mi}$ to $(a_0/v^*)_{Mi}$. For non-polar components, it turns out that there exists a near-universal relation

$$a'/(v^* RT) = C [a_0/(v^* RT)]^2, \tag{16}$$

where $C$ is a weak function of the antisphericity parameter. Consequently, for mixtures of non-polar components one may split $(a'/v^*)_{Mi}$ and $(a_0/v^*)_{Mi}$ into the contributions from like and unlike interactions, e.g.

$$(a_0/v^*)_{Mi} = x_1^2 (a_0/v^*)_{11} + 2 x_1 x_2 (a_0/v^*)_{12} + x_2^2 (a_0/v^*)_{22}, \tag{17}$$

and to relate

$$\left( \frac{a'}{v^* RT} \right)_{12} = \frac{C_{11} + C_{22}}{2} \left( \frac{a_0}{v^* RT} \right)_{12}^2. \tag{18}$$

For mixtures of polar + non-polar components this prescription breaks down, because the dipole-dipole interaction gives rise to a smaller (and slightly temperature dependent) $C$ in equ. (16). But the unlike interaction contains only dispersion and induction energies, so the mixed $C$ of equ. (18) should be of the order of $C_{non-polar}$. Therefore, it was suggested [18] for polar + non-polar mixtures to take for $C_{12}$ the value of $C$ of the non-polar component, but corrected for the mixed antisphericity parameter, which is

$$\alpha_{12} = \frac{(R_1^* + R_2^*) (S_1^* + S_2^*)}{6 (V_1^* + V_2^*)} \tag{19}$$

with $R_i^*$, $S_i^*$ und $V_i^*$ being mean curvature, surface and volume of molecule $i$, quantities to be derived from the molecular model. For the correction it is assumed that

$$dC/d\alpha \approx -0.001. \tag{20}$$

Table 12 gives a summary of the input data for the calculation. The result is $g_{0.5}^E = 1\,624$ for 293.15 K and $g_{0.5}^E = 1\,602$ for 313.15 K, and $h_{0.5}^E (303.15\,K) = 1\,947\,J\,mol^{-1}$. This is the experimental value of $h^E$, but the calculated $g^E$-value is about 17% too high. Nevertheless, it is not too bad for a first estimate for such a complicated mixture.

   A by-product of the calculation of excess properties by the equation of state is the isothermal compressibility of the mixture. For $x_2 = 0.51$, the calculated value is $\beta_T = 1\,024\,TPa^{-1}$ (for 293.15 K), to be compared to the experimental value [20] of $\beta_T = 1\,035\,TPa^{-1}$. The discrepancy of 1% is of the same order as the experimental uncertainty.

Table 12. *Input data for application of the equation of state concept [18] to chlorex + isooctane ($p_\sigma$: vapour pressure at saturation curve, $\beta_T$: isothermal compressibility, B: second virial coefficient, R\*, S\* and V\*: mean curvature, surface and volume of the molecule as derived from the molecular model)*

| Chlorex | Isooctane |
| --- | --- |
| 293.15 K | 293.15 K |
| $v = 117.585 \, cm^3 \, mol^{-1}$ | $v = 165.101 \, cm^3 \, mol^{-1}$ |
| $\beta_T = 613.7 \, TPa^{-1}$ [20] | $\beta_T = 1476 \, TPa^{-1}$ [20, 21] |
| $p_\sigma = 0.0001513 \, MPa$ | $p_\sigma = 0.005150 \, MPa$ |
| $B = -6300 \, cm^3 \, mol^{-1}$ | $B = -2980 \, cm^3 \, mol^{-1}$ |
| molecular model: | molecular model: |
|   furanoid structure [23] |   irregular polyhedron [19] |
| $R^* = 3.2559 \, \text{Å}$ | $R^* = 3.4861 \, \text{Å}$ |
| $S^* = 120.852 \, \text{Å}^2$ | $S^* = 140.311 \, \text{Å}^2$ |
| $V^* = 107.361 \, \text{Å}^3$ | $V^* = 140.524 \, \text{Å}^3$ |
| 313.15 K | 313.15 K |
| $v = 119.928 \, cm^3 \, mol^{-1}$ | $v = 169.137 \, cm^3 \, mol^{-1}$ |
| $p_\sigma = 0.0004941 \, MPa$ | $p_\sigma = 0.012959 \, MPa$ |
| $B = -5700 \, cm^3 \, mol^{-1}$ | $B = -2500 \, cm^3 \, mol^{-1}$ |
| $R^* = 3.2505 \, \text{Å}$ | $R^* = 3.4752 \, \text{Å}$ |
| $S^* = 120.4104 \, \text{Å}^2$ | $S^* = 139.362 \, \text{Å}^2$ |
| $V^* = 106.7095 \, \text{Å}^3$ | $V^* = 139.007 \, \text{Å}^3$ |

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