

EFFECT OF TEMPERATURE AND CHAIN LENGTH OF THE ALKANE ON  $H^E$  OF  
2-METHOXYETHANOL+ALKANE MIXTURES

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SUMMARY

Experimental results of the composition dependence of the molar excess enthalpy  $H^E$  are reported for binary mixtures of some alkanes with 2-methoxyethanol at 323, 348 and 373 K and pressures up to 25 bar. The effect of size and shape of the alkane molecule on  $H^E$  and the dependence of  $H^E$  on temperature are discussed.

The experimental results can be described with a modified form of the UNIFAC-model combined with an association term taking into account the H-bonding of 2-methoxyethanol. The MUNIQUAC-RAS-model used is explained; its system-specific parameters vary systematically with temperature and with size and shape of the alkanes mixed with 2-methoxyethanol.

INTRODUCTION

Fluid phase equilibria and thermodynamic excess properties of mixtures consisting of a selfassociating component and an inert solvent can be described most adequately by theoretical models which account for multiple association due to hydrogen bonding (ref. 1-4). These models, however, so far are not flexible enough to describe different properties with the same set of system-specific model parameters (ref. 5, 6). Therefore good experimental data are required at varying state conditions for many more appropriate mixtures in order to test the applicability and to improve theoretical models for predicting the thermodynamic behaviour of fluids and their mixtures. Without reliable predictions proper design of separation processes is impossible.

In this paper experimental results of  $H^E$  are reported for binary mixtures of 2-methoxyethanol with the following alkanes: n-hexane, n-heptane, n-octane, n-decane and 2,2,4-trimethylpentane. Using the MUNIQUAC-model proposed by Bijl, de Loos and Lichtenthaler (ref. 7) combined with the linear association (RAS) model according to Renon and Prausnitz (ref. 8) the dependence of  $H^E$  on composition and temperature can be represented very well. An empirical correlation of the system-specific model parameters could be developed allowing the calculation of  $H^E$  at any

state condition within the ranges investigated. 2-methoxyethanol is a polar, self-associating solvent widely used in industry and therefore such calculations are also of interest for practical application.

## EXPERIMENTAL

### Apparatus

The quasi-isothermal flow calorimeter (Model 7501 from HART SCIENTIFIC, Utah, USA) has been described elsewhere (ref. 6, 9) and therefore only a short summary of the experimental procedure is given here.

Fig.1 shows schematically the set-up of the calorimeter. The two pure components

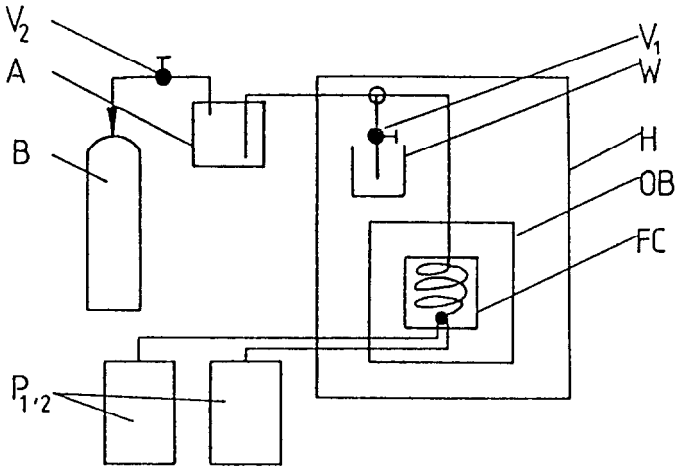


Fig. 1. Schematic diagram of the flow calorimeter.  $P_{1,2}$ =VARIAN-pumps, FC=flow cell, OB=thermostatted oil bath H=hood, W=waste box,  $V_1, V_2$ =valves, A=autoclave, B=nitrogen bomb.

to be mixed are pumped continuously by two precision high pressure syringe pumps  $P_{1,2}$  (VARIAN 8500) into a mixing coil sitting in a flow cell FC. FC is immersed in an oil bath OB thermostatted at the temperature the mixing process is taking place. A Peltier cooler removes with constant rate energy from FC and a pulsed control-heater compensates for this energy and for the energy liberated (exothermic) or absorbed (endothermic) by the mixing process. In this way the temperature of the flow cell and consequently that one of the mixture formed are maintained at the constant temperature of OB (quasi-isothermal operation). The mixture leaves OB and flows into an autoclave A, which contains nitrogen kept at that pressure the measurement is performed. The volume of A is so large ( $\sim 2000 \text{ cm}^3$ ) that during one measurement

the change in pressure due to the decrease in volume by entering liquid mixture ( $\sim 30 \text{ cm}^3$ ) usually is negligible. Through valve  $V_1$  the liquid mixture can be removed from A after each measurement.

The energy supplied by the control-heater before (or after) and during a mixing process keeping the temperature of FC constant is a direct measure of the energy of mixing. Knowing the volumetric flowrates delivered, the molar masses and densities of the pure components the mole fraction of the mixture obtained in the mixing coil can be calculated. Just as well the corresponding molar excess enthalpy can be calculated from these data and the measured change in heating power before and during the continuous mixing process at the temperature and pressure the experiment is performed. Measurements with various flow rates give different compositions of the mixture formed and therefore the dependence of  $H^E$  on mole fraction can be determined. The calorimeter described can be used in the temperature range 20–200°C for pressures up to 150 bar.

### Results and Discussion

The substances used in this work were obtained from standard laboratory supply sources and the purity was at least 99.5 Vol%. They were used without further purification. However, 2-methoxyethanol was dried with molecular sieve and kept under nitrogen in order to avoid oxidation.

The results of  $H^E$  at 323, 348 and 373 K for all mixtures investigated are given in Tables 1–3 respectively. The pressure usually is 1 bar except at the higher temperatures where the measurements had to be performed at pressures up to 25 bar for some of the mixtures in order to avoid the formation of a vapour phase. The actual pressure is always given in brackets in the headings in Tables 1–3. Some measurements performed at 150 bar revealed that the effect of pressure on  $H^E$  at the temperatures and for the mixtures investigated is rather small. At 15 bar and 25 bar the effect is below 0.5% in the entire mole fraction range and therefore it can be neglected within the estimated inaccuracy of the experiments:  $\pm 2\%$  in  $H^E$  and  $\pm 5 \cdot 10^{-4}$  in the mole fraction.

The  $H^E$ -values are for all mixtures positive (endothermic mixing). Figs. 2–4 show the composition dependence for some selected mixtures at various temperatures. In all cases it was possible to represent the dependence of  $H^E$  on mole fraction with the Redlich-Kister Equation:

$$H^E(x) = x(1-x) \sum_{m=0}^n A_m (2x-1)^m \quad (1)$$

with  $x$  being the mole fraction of 2-methoxyethanol. Up to 7 coefficients  $A_m$  were necessary to give such a good description of  $H^E$  as shown in Figs. 2-4. The Redlich-Kister constants  $A_m$  at the various temperatures together with the standard deviation  $\delta(H^E)$  obtained by the method of least squares with all data points weighed equally are given in Table 4.

TABLE 1. Experimental results of the molar excess enthalpy for  
2-methoxyethanol + alkane mixtures at 323.15 K

| $x$   | $\frac{H^E}{J \cdot \text{mol}^{-1}}$ | $x$    | $\frac{H^E}{J \cdot \text{mol}^{-1}}$ |
|---|---------------------------------------|--------|---------------------------------------|
| x 2-methoxyethanol + (1-x) C <sub>6</sub> H <sub>14</sub> (1 bar) |                                       |        |                                       |
| 0.0761  | 767                                   | 0.5798 | 1327                                  |
| 0.1308  | 992                                   | 0.6222 | 1286                                  |
| 0.1414  | 1037                                  | 0.6986 | 1184                                  |
| 0.2030  | 1192                                  | 0.7671 | 1050                                  |
| 0.2478  | 1253                                  | 0.8317 | 866                                   |
| 0.3541  | 1353                                  | 0.8917 | 631                                   |
| 0.4516  | 1368                                  | 0.9479 | 341                                   |
| 0.5405  | 1344                                  |        |                                       |
| x 2-methoxyethanol + (1-x) C <sub>7</sub> H <sub>16</sub> (1 bar) |                                       |        |                                       |
| 0.1102  | 929                                   | 0.6501 | 1375                                  |
| 0.1445  | 1040                                  | 0.6990 | 1326                                  |
| 0.2709  | 1351                                  | 0.7223 | 1299                                  |
| 0.3824  | 1453                                  | 0.7879 | 1126                                  |
| 0.4816  | 1466                                  | 0.8479 | 932                                   |
| 0.5703  | 1453                                  | 0.9028 | 685                                   |
| 0.5978  | 1432                                  | 0.9533 | 380                                   |
| x 2-methoxyethanol + (1-x) 2,2,4-trimethylpentane (1 bar)         |                                       |        |                                       |
| 0.0651  | 735                                   | 0.5108 | 1401                                  |
| 0.1040  | 963                                   | 0.5987 | 1335                                  |
| 0.1222  | 1036                                  | 0.6762 | 1274                                  |
| 0.1596  | 1155                                  | 0.7451 | 1148                                  |
| 0.1728  | 1188                                  | 0.8068 | 1008                                  |
| 0.2946  | 1399                                  | 0.8624 | 828                                   |
| 0.3170  | 1418                                  | 0.9038 | 643                                   |
| 0.3852  | 1457                                  | 0.9126 | 595                                   |
| 0.4104  | 1439                                  | 0.9583 | 317                                   |

TABLE 2. Experimental results of the molar excess enthalpy for  
2-methoxyethanol + alkane mixtures at 348.15 K

| x  | $\frac{H^E}{J \cdot \text{mol}^{-1}}$ | x      | $\frac{H^E}{J \cdot \text{mol}^{-1}}$ | x      | $\frac{H^E}{J \cdot \text{mol}^{-1}}$ |
|--|---------------------------------------|--------|---------------------------------------|--------|---------------------------------------|
| x 2-methoxyethanol + (1-x) C <sub>6</sub> H <sub>14</sub> (15 bar) |                                       |        |                                       |        |                                       |
| 0.0538   | 714                                   | 0.4517 | 1706                                  | 0.7672 | 1216                                  |
| 0.1053   | 1102                                  | 0.5407 | 1644                                  | 0.8318 | 989                                   |
| 0.1303   | 1236                                  | 0.6223 | 1541                                  | 0.9477 | 370                                   |
| 0.2479   | 1589                                  | 0.6976 | 1398                                  | 0.9795 | 149                                   |
| 0.3546   | 1711                                  |        |                                       |        |                                       |
| x 2-methoxyethanol + (1-x) C <sub>7</sub> H <sub>16</sub> (1 bar)  |                                       |        |                                       |        |                                       |
| 0.0406   | 562                                   | 0.3959 | 1816                                  | 0.8288 | 1148                                  |
| 0.1170   | 1142                                  | 0.4707 | 1805                                  | 0.8925 | 833                                   |
| 0.1874   | 1447                                  | 0.5804 | 1722                                  | 0.9492 | 437                                   |
| 0.2833   | 1706                                  | 0.6748 | 1578                                  | 0.9903 | 60                                    |
| 0.3416   | 1764                                  | 0.7568 | 1389                                  |        |                                       |
| x 2-methoxyethanol + (1-x) C <sub>8</sub> H <sub>18</sub> (1 bar)  |                                       |        |                                       |        |                                       |
| 0.0976   | 1132                                  | 0.5253 | 1882                                  | 0.8274 | 1185                                  |
| 0.1859   | 1569                                  | 0.5780 | 1804                                  | 0.8915 | 866                                   |
| 0.3394   | 1875                                  | 0.6727 | 1650                                  | 0.9487 | 468                                   |
| 0.4065   | 1915                                  | 0.7550 | 1441                                  |        |                                       |
| x 2-methoxyethanol + (1-x) C <sub>10</sub> H <sub>22</sub> (1 bar) |                                       |        |                                       |        |                                       |
| 0.1148   | 1291                                  | 0.5135 | 1934                                  | 0.7870 | 1402                                  |
| 0.2149   | 1778                                  | 0.6215 | 1799                                  | 0.9079 | 866                                   |
| 0.3030   | 1988                                  | 0.7113 | 1607                                  | 0.9568 | 474                                   |
| 0.3811   | 2039                                  |        |                                       |        |                                       |
| x 2-methoxyethanol + (1-x) 2,2,4-trimethylpentane (1 bar)          |                                       |        |                                       |        |                                       |
| 0.1596   | 1303                                  | 0.5987 | 1593                                  | 0.8624 | 898                                   |
| 0.2946   | 1686                                  | 0.6762 | 1451                                  | 0.9126 | 671                                   |
| 0.4104   | 1779                                  | 0.7451 | 1292                                  | 0.9583 | 354                                   |
| 0.5108   | 1704                                  | 0.8068 | 1111                                  |        |                                       |

TABLE 3. Experimental results of the molar excess enthalpy for  
2-methoxyethanol + alkane mixtures at 373.15 K

| x  | $\frac{H^E}{J \cdot \text{mol}^{-1}}$ | x      | $\frac{H^E}{J \cdot \text{mol}^{-1}}$ | x      | $\frac{H^E}{J \cdot \text{mol}^{-1}}$ |
|--|---------------------------------------|--------|---------------------------------------|--------|---------------------------------------|
| x 2-methoxyethanol + (1-x) C <sub>6</sub> H <sub>14</sub> (25 bar) |                                       |        |                                       |        |                                       |
| 0.0407   | 555                                   | 0.5502 | 1938                                  | 0.7943 | 1242                                  |
| 0.1912   | 1655                                  | 0.6234 | 1778                                  | 0.8688 | 859                                   |
| 0.3246   | 1976                                  | 0.7129 | 1554                                  | 0.9371 | 402                                   |
| 0.4435   | 2040                                  |        |                                       |        |                                       |
| x 2-methoxyethanol + (1-x) C <sub>7</sub> H <sub>16</sub> (15 bar) |                                       |        |                                       |        |                                       |
| 0.0364   | 529                                   | 0.3687 | 2167                                  | 0.7350 | 1642                                  |
| 0.1056   | 1248                                  | 0.4421 | 2184                                  | 0.8119 | 1319                                  |
| 0.1704   | 1662                                  | 0.5521 | 2084                                  | 0.9433 | 485                                   |
| 0.2605   | 2001                                  | 0.6490 | 1897                                  |        |                                       |
| x 2-methoxyethanol + (1-x) C <sub>8</sub> H <sub>18</sub> (1 bar)  |                                       |        |                                       |        |                                       |
| 0.0976   | 1233                                  | 0.5253 | 2242                                  | 0.8274 | 1356                                  |
| 0.1859   | 1827                                  | 0.5780 | 2166                                  | 0.8915 | 969                                   |
| 0.3394   | 2253                                  | 0.6727 | 1953                                  | 0.9487 | 516                                   |
| 0.4065   | 2312                                  | 0.7550 | 1679                                  |        |                                       |
| x 2-methoxyethanol + (1-x) C <sub>10</sub> H <sub>22</sub> (1 bar) |                                       |        |                                       |        |                                       |
| 0.1148   | 1422                                  | 0.5135 | 2437                                  | 0.7870 | 1718                                  |
| 0.2149   | 2049                                  | 0.6215 | 2264                                  | 0.9079 | 969                                   |
| 0.3030   | 2346                                  | 0.7113 | 2010                                  | 0.9568 | 507                                   |
| 0.3811   | 2463                                  |        |                                       |        |                                       |
| x 2-methoxyethanol + (1-x) 2,2,4-trimethylpentane (10 bar)         |                                       |        |                                       |        |                                       |
| 0.1603   | 1589                                  | 0.5999 | 1980                                  | 0.8630 | 1021                                  |
| 0.2957   | 2049                                  | 0.6773 | 1801                                  | 0.9130 | 689                                   |
| 0.4117   | 2161                                  | 0.7461 | 1582                                  | 0.9585 | 327                                   |
| 0.5121   | 2110                                  | 0.8076 | 1309                                  |        |                                       |

TABLE 4. Coefficients  $A_m/J^*\text{mol}^{-1}$  and standard deviations  $\delta(H^E)$  for least-squares representation of  $H^E/J^*\text{mol}^{-1}$  for 2-methoxy-ethanol + alkane by eqn. (1) at 323.15, 348.15 and 373.15 K.

323.15 K

| 2-methoxy-ethanol +              | $C_6H_{14}$ | $C_7H_{16}$ | $C_8H_{18}$ | $C_{10}H_{22}$ | 2,2,4-trimethylpentane |
|----------------------------------|-------------|-------------|-------------|----------------|------------------------|
| $A_0$                            | 5469.7      | 5881.3      |             |                | 5640.0                 |
| $A_1$                            | -650.5      | -141.3      |             |                | -1208.7                |
| $A_3$                            | 2361.2      | 3198.5      |             |                | 4086.1                 |
| $A_4$                            | -171.2      | -1471.3     |             |                | 1838.6                 |
| $A_5$                            | 2985.9      | 1766.8      |             |                | -1483.1                |
| $A_6$                            | -3062.4     |             |             |                | -4718.1                |
| $A_7$                            |             |             |             |                | 4710.0                 |
| $\delta(H^E)/J^*\text{mol}^{-1}$ | 8.8         | 12.5        |             |                | 6.8                    |

348.15 K

| 2-methoxy-ethanol +              | $C_6H_{14}$ | $C_7H_{16}$ | $C_8H_{18}$ | $C_{10}H_{22}$ | 2,2,4-trimethylpentane |
|----------------------------------|-------------|-------------|-------------|----------------|------------------------|
| $A_0$                            | 6720.9      | 7181.5      | 7565.9      | 7858.7         | 6843.6                 |
| $A_1$                            | -1150.6     | -1386.0     | -1177.1     | -2138.4        | -2000.2                |
| $A_2$                            | 3137.3      | 2986.1      | 3139.1      | 4208.6         | 3640.8                 |
| $A_3$                            | -2669.1     | 2265.6      | -1687.3     | 525.0          | 869.8                  |
| $A_4$                            | 2176.7      | 2634.1      | 3125.4      | 2493.7         |                        |
| $A_5$                            |             | -4729.4     |             |                |                        |
| $\delta(H^E)/J^*\text{mol}^{-1}$ | 15.2        | 13.4        | 11.6        | 12.1           | 14.4                   |

373.15 K

| 2-methoxy-ethanol +              | $C_6H_{14}$ | $C_7H_{16}$ | $C_8H_{18}$ | $C_{10}H_{22}$ | 2,2,4-trimethylpentane |
|----------------------------------|-------------|-------------|-------------|----------------|------------------------|
| $A_0$                            | 7962.5      | 8585.8      | 9081.8      | 9804.9         | 8467.2                 |
| $A_1$                            | -2087.1     | -1689.3     | -1785.7     | -1682.8        | -1685.7                |
| $A_2$                            | 3021.9      | 3408.1      | 3557.8      | 3766.7         | 3748.6                 |
| $A_3$                            | 215.7       | -1603.8     | -931.6      | -143.3         | -1580.1                |
| $A_4$                            | 12.9        | 861.4       | 1581.5      | 1570.9         | -262.8                 |
| $A_5$                            | -3201.7     |             |             |                |                        |
| $\delta(H^E)/J^*\text{mol}^{-1}$ | 14.3        | 6.3         | 4.8         | 5.4            | 10.6                   |

As shown in Fig. 2 at 373 K the endothermic  $H^E$ -values are increasing with increasing number of C-atoms in the n-alkane, i.e. with increasing chain length. Analogous behaviour is found at 323 K and 348 K.

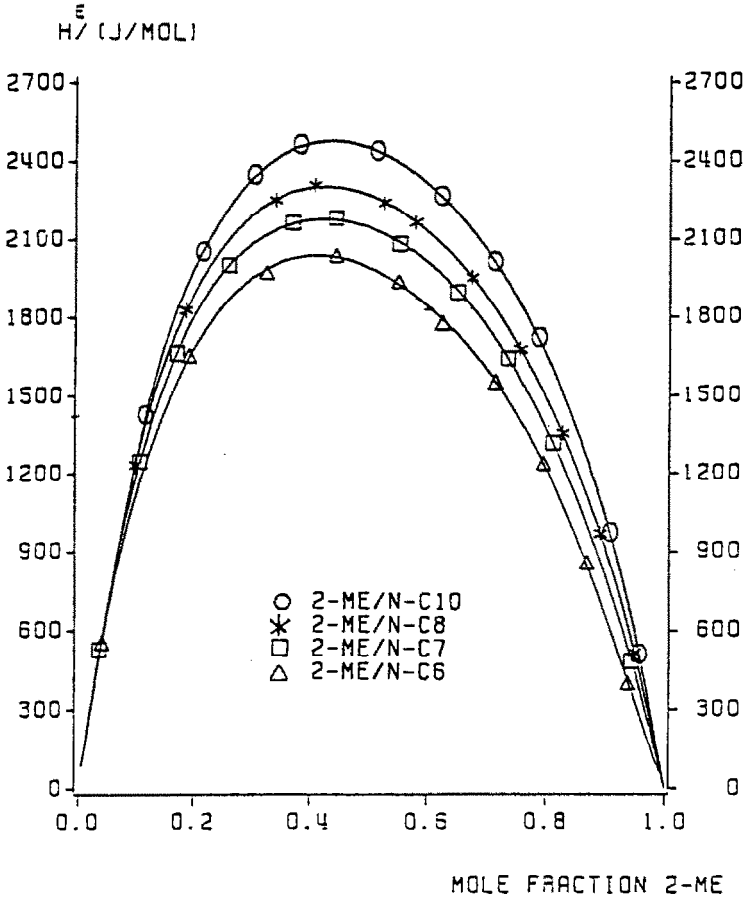


Fig. 2. Effect of chain length of the n-alkane component on  $H^E$  at 373.15 K for x 2-methoxyethanol+(1-x) alkane:  $\Delta$  n-hexane at 25 bar,  $\square$  n-heptane at 15 bar,  $*$  n-octane at 1 bar,  $\circ$  n-decane at 1 bar. Curves calculated with eqn. (1) using coefficients from Table 4.

For the mixture with the branched alkane the  $H^E$ -values are less endothermic with respect to the values for the mixture with the corresponding n-alkane. This is shown in Fig. 3, where the dependence of  $H^E$  on mole fraction at 373 K for the mixture with 2,2,4-trimethylpentane is nearly the same as the one for the mixture with



n-heptane. Branching makes an alkane molecule more compact and it is behaving like a shorter n-alkane.

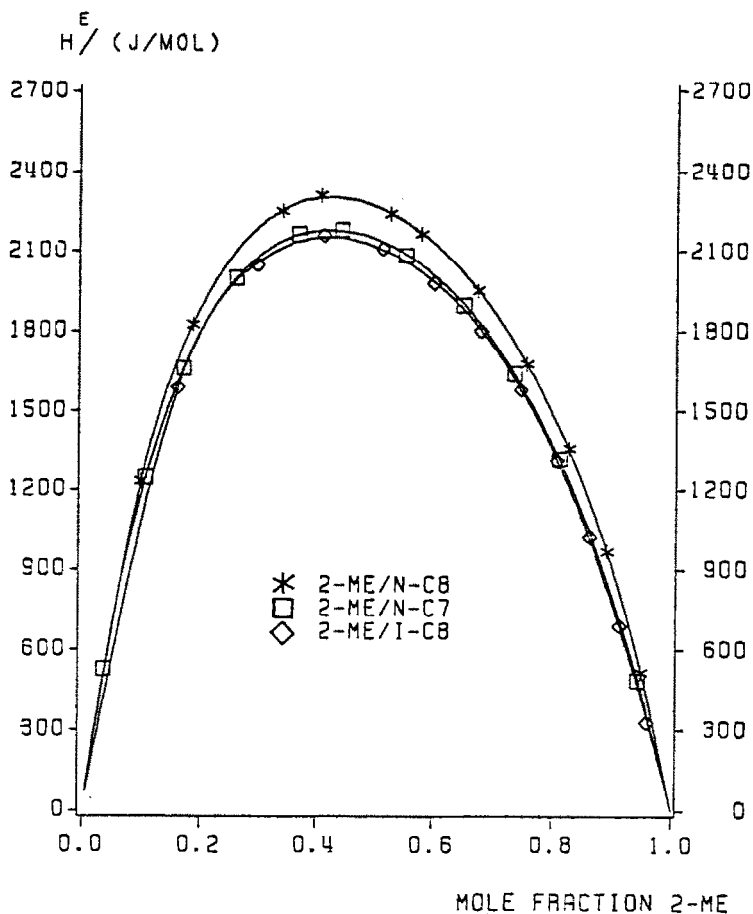


Fig. 3. Effect of branching of the alkane component on  $H^E$  at 373.15K for x 2-methoxyethanol+(1-x)alkane: □ n-heptane at 15 bar, ◇ 2,2,4-trimethylpentane at 10 bar, \* n-octane at 1 bar. Curves calculated with eqn. (1) using coefficients from Table 4.

A similar effect of branching has been observed for the upper critical solution temperature (UCST) of the liquid-liquid-equilibria which 2-methoxyethanol+alkane mixtures show at lower temperatures (ref. 7). The shorter and the more branched an alkane molecule is the lower is UCST. The mixtures of 2-methoxyethanol with n-heptane and 2,2,4-trimethylpentane respectively nearly have the same UCST at 1 bar.

In Fig. 4 the strong effect of temperature on  $H^E$  is shown, as an example, for the mixture 2-methoxyethanol+n-hexane. Changing the temperature from 323 K to 373 K changes the maximum of  $H^E$  from about 1370 J\* $\text{mol}^{-1}$  to about 2040 J\* $\text{mol}^{-1}$ . This behaviour is typical for mixtures of an associating and an inert component and it is due to the change in the difference of the number of the H-bonds the associating component forms in its pure state and in the mixture (ref. 10, 11). Analogous behaviour is observed for all the other mixtures investigated.

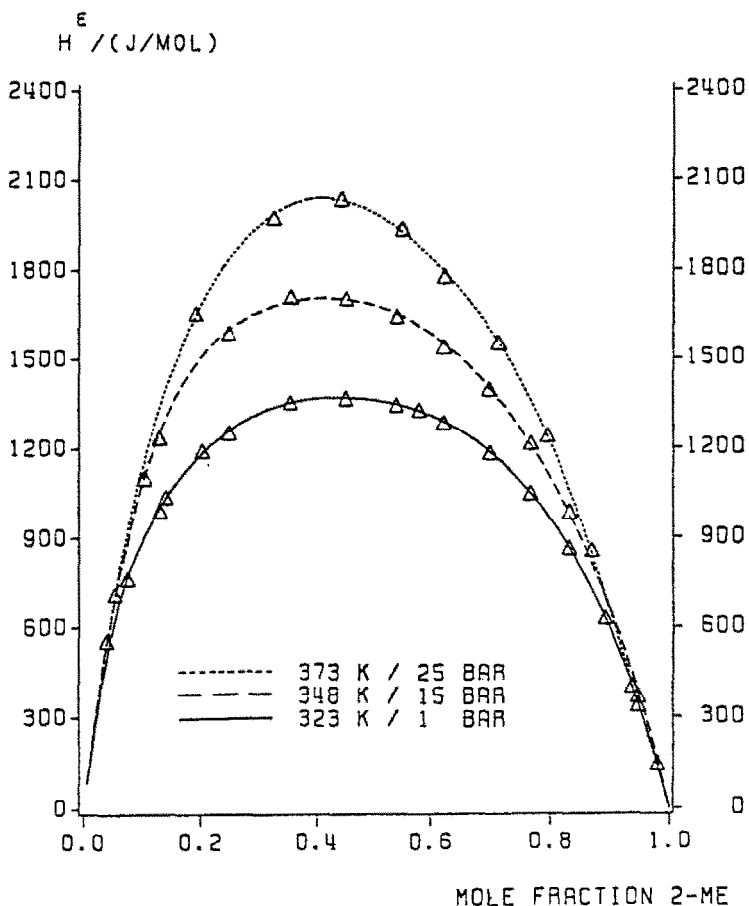


Fig. 4. Effect of temperature on  $H^E$  for  $x$  2-methoxyethanol+(1-x) n-hexane: — 323.15 K, 1 bar; ---348.15 K, 15 bar; .....373.15 K, 25 bar. Curves calculated with eqn. (1) using coefficients from Table 4.

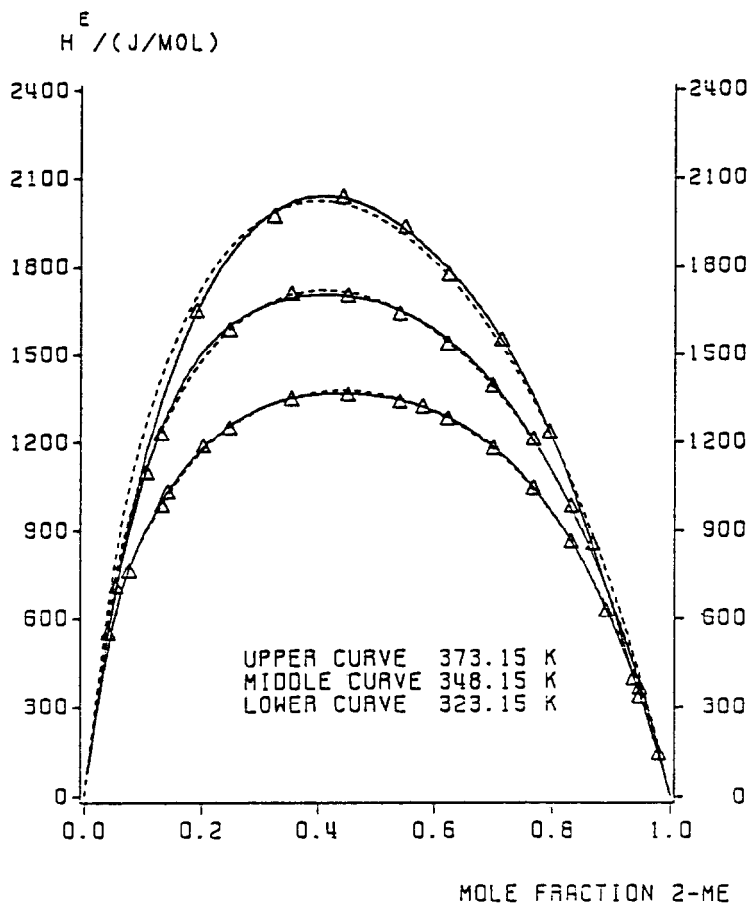


Fig. 5. Comparison between calculated and experimental  $H^E$ -values for  $x$  2-methoxyethanol+(1- $x$ )  $n$ -hexane at various temperatures: --- MUNIQAC-RAS model — Redlich-Kister fit,  $\Delta$  experiment.

The temperature dependence of  $\Delta U_{12} \equiv \Delta U_{AB}$  and  $\Delta U_{21} \equiv \Delta U_{BA}$  is shown in Fig. 6 for the mixtures with  $n$ -alkanes. Both parameters vary systematically when going from  $n$ -hexane to  $n$ -decane. Whereas  $\Delta U_{12}$  increases with increasing number  $n$  of C-atoms of the  $n$ -alkane  $\Delta U_{21}$  decreases in the entire temperature range covered. At a particular temperature this dependence on  $n$  can be very well represented by the following equations:

Just so as H-bonding of the 2-methoxyethanol molecules determines the dependence of  $H^E$  on temperature it is also responsible for the relatively large endothermic  $H^E$ -values obtained. At a given temperature, however, the dependence of  $H^E$  on the chain length and the degree of branching can be explained by the existence of some kind of short range order (CMO) in liquids with chain-like molecules (ref. 12-14). The CMO (Correlation of Molecular Orders) can be interpreted as a packing effect between groups of segments of different n-alkane molecules, being the more pronounced the longer the chain-like molecule is. Upon mixing with a compact molecule like 2-methoxyethanol the CMO is destroyed gradually, depending on the composition of the mixture. The energy associated leads to an endothermic contribution to  $H^E$ , which increases with increasing CMO. That is the reason why, as shown in Fig. 2,  $H^E$  increases stronger with increasing chain length than expected from the changes in the intermolecular interactions when going from n-hexane to n-decane. In n-hexane CMO is less pronounced as in n-decane and therefore the corresponding endothermic  $H^E$ -contribution is smaller for the mixture with n-hexane than for the mixture with n-decane. Due to steric hinderance pure branched alkanes show only little or no CMO. Therefore for mixtures of branched isomeric alkanes smaller  $H^E$ -values are observed than for the mixture with the corresponding n-alkane. The CMO-contribution becomes smaller the more branched an alkane molecule is and for that reason, as shown in Fig. 3,  $H^E$  for the mixture with 2,2,4-trimethylpentane is smaller than  $H^E$  for the mixture with n-octane.

## CALCULATIONS

### The MUNIQUAC-RAS model

Models for calculating thermodynamic excess properties of mixtures containing associating components usually express these properties as the sum of a physical and a chemical contribution. The physical contribution depends on the dispersion forces between the various molecules whereas the chemical contribution results from the association by H-bonding (ref. 1, 2, 11). This approach is also used in this work for  $H^E$ :

$$H^E = H^E_{\text{phys}} + H^E_{\text{chem}} \quad (2)$$

For  $H^E_{\text{phys}}$  a modification of the UNIQUAC-model is chosen. This so-called MUNIQUAC-model was developed by Bijl, de Loos and Lichtenthaler especially for correlating liquid-liquid-equilibria of binary mixtures of 2-methoxyethanol with various alkanes (ref. 7). As these are the same mixtures as investigated in this work it therefore was obvious to combine this model with a proper expression for  $H^E_{\text{chem}}$ . For  $H^E_{\text{chem}}$  the real-associated-solution (RAS)-model proposed by Renon and Prausnitz (ref. 8) is chosen, which successfully has been used by various authors

in combined models (ref. 1, 2). In the MUNIQUAC-model for binary mixtures of components 1 and 2 the following relations between local ( $\theta_{12}, \theta_{21}$ ) and overall surface fractions ( $\theta_1, \theta_2$ ) are used:

$$\frac{\theta_{21}}{\theta_{11}} = \frac{\theta_2}{\theta_1} \exp \left( - \frac{\theta_2}{\theta_1} \frac{\Delta U_{21}}{RT} \right) \quad (3)$$

$$\frac{\theta_{12}}{\theta_{22}} = \frac{\theta_1}{\theta_2} \exp \left( - \frac{\theta_1}{\theta_2} \frac{\Delta U_{12}}{RT} \right) \quad (4)$$

where  $\Delta U_{21}$  and  $\Delta U_{12}$  are system-specific model parameters, R is the universal gas constant and T the temperature. These relations are different from the ones originally proposed by Abrams and Prausnitz (ref. 15) by the ratios  $\theta_2/\theta_1$  and  $\theta_1/\theta_2$  within the exp-terms in eqns. (3) and (4) respectively. With eqns. (3) and (4) the local and overall surface fractions are approaching each other asymptotically, if in a mixture  $\theta_2/\theta_1$  or  $\theta_1/\theta_2$  are going to zero. In other words the exponents in the exp-terms are approaching zero, if a mixture is becoming very diluted, i.e. the ideal behaviour at infinite dilution of any real mixture is approached asymptotically. Following Maurer and Prausnitz (ref. 16) but using eqns. (3) and (4) the residual part of the excess Gibbs energy  $G_{res}^E$  for the MUNIQUAC-model is obtained as:

$$\begin{aligned} \frac{G_{res}^E}{RT} = & -x_1 q_1 \frac{\theta_1}{\theta_2} \ln \left[ \theta_1 + \theta_2 \exp \left( - \frac{\theta_2}{\theta_1} \frac{\Delta U_{21}}{RT} \right) \right] \\ & - x_2 q_2 \frac{\theta_2}{\theta_1} \ln \left[ \theta_2 + \theta_1 \exp \left( - \frac{\theta_1}{\theta_2} \frac{\Delta U_{12}}{RT} \right) \right] \end{aligned} \quad (5)$$

where  $q_1$  and  $q_2$  are pure-component molecular-structure constants depending on molecular size and surface area.  $x_1$  and  $x_2$  are the mole fraction of component 1 and 2 respectively. Surface fractions  $\theta_1$  and  $\theta_2$  are given by:

$$\theta_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} = 1 - \theta_2 \quad (6)$$

Therefore the only parameters which have to be fitted are  $\Delta U_{12}$  and  $\Delta U_{21}$ . Assuming these parameters to be independent of temperature the thermodynamic relation

$$\frac{\delta(G_{\text{res}}^E/T)}{\delta T} = - \frac{H_{\text{phys}}^E}{T^2} \quad (7)$$

yields the following expression for  $H_{\text{phys}}^E$ :

$$H_{\text{phys}}^E = \frac{x_1 q_1 \theta_2 \Delta U_{21} \exp\left(-\frac{\theta_2}{\theta_1} \frac{\Delta U_{21}}{RT}\right)}{\theta_1 + \theta_2 \exp\left(-\frac{\theta_2}{\theta_1} \frac{\Delta U_{21}}{RT}\right)} + \frac{(1-x_1) q_2 \theta_1 \Delta U_{12} \exp\left(-\frac{\theta_1}{\theta_2} \frac{\Delta U_{12}}{RT}\right)}{\theta_2 + \theta_1 \exp\left(-\frac{\theta_1}{\theta_2} \frac{\Delta U_{12}}{RT}\right)} \quad (8)$$

With this equation  $\Delta H_{\text{phys}}^E$  can be calculated using only pure component data as soon as  $\Delta U_{21}$  and  $\Delta U_{12}$  are determined.

The RAS-model (ref. 8) gives the following expression for  $H_{\text{chem}}^E$ :

$$H_{\text{chem}}^E = x_1 K_1 \Delta h_1^* (\varphi_{1,\text{mon}} - \varphi_{1,\text{mon}}^0) \quad (9)$$

where index 1 refers to the associating component. Assuming linear consecutive association the association constant is defined as:

$$K_1 = \frac{c_i}{c_{i-1} * c_1} \frac{1}{V_1} \quad (10)$$

$K_1$  is regarded to be independent of  $i$  with  $c_i$  being the molar concentration of  $i$ -mers consisting of  $i$  associated molecules and  $V_1$  being the molar volume of component 1. According to this definition  $K_1$  is a dimensionless quantity.  $\Delta h_1^*$  is the

change in energy associated with the formation of one mole H-bonds.  $x_1$  is the overall mole fraction and  $\varphi_{1,\text{mon}}$  and  $\varphi_{1,\text{mon}}^0$  are the volume fractions of monomers (non-associated molecules) in the mixture and the pure liquid respectively.  $\varphi_{1,\text{mon}}$  and  $\varphi_{1,\text{mon}}^0$  can be calculated with the following equation:

$$\varphi_{1,\text{mon}} = \frac{1 + 2K_1\Phi_1 - \sqrt{(1 + 4K_1\Phi_1)}}{2K_1^2\Phi_1} \quad (11)$$

(with  $\varphi_{1,\text{mon}} = \varphi_{1,\text{mon}}^0$  for  $\Phi_1 = 1$ )

In this equation  $\Phi_1$  is the overall volume fraction given by:

$$\Phi_1 = \frac{x_1V_1}{x_1V_1 + x_2V_2} \quad (12)$$

with  $V_2$  being the molar volume of component 2.

The temperature dependence of  $K_1$  can be written as:

$$K_1 = K_1^0 \exp\left(\frac{\Delta h_1^*}{RT} \left(-\frac{1}{T} - \frac{1}{T^0}\right)\right) \quad (13)$$

with  $K_1^0$  being the numerical value at temperature  $T^0$ .

With these equations  $\Delta H_{\text{chem}}^E$  can be calculated using only pure component data as soon as  $K_1^0$  and  $\Delta h_1^*$  are determined. Except for pure component constants the MUNIQUAC-RAS model obtained by using eqn. (8) and eqn. (9) with eqn. (2) gives an expression for  $H^E$  with the four system-specific parameters  $\Delta U_{21}$ ,  $\Delta U_{12}$ ,  $K_1^0$  and  $\Delta h_1^*$ .

#### Determination of model parameters

The system-specific parameters of the model used can be obtained by fitting the theoretical expression for  $H^E$  to experimental data. In order to determine  $K_1^0$  and  $\Delta h_1^*$  only the  $H^E$ -data at 348 K were used. At this temperature all four parameters  $K_1^0$ ,  $\Delta h_1^*$ ,  $\Delta U_{12}$  and  $\Delta U_{21}$  were fitted simultaneously to the data with pure component constants  $q_1$  and  $q_2$  taken from literature (ref. 17). It was found that for all mixtures the same values of  $K_1^0$  and  $\Delta h_1^*$  can be used:

$$K_1^0 (T^0 = 348.15 \text{ K}) = 29.1$$

$$\Delta h_1^* = -29.3 \text{ kJ}\cdot\text{mol}^{-1}$$

These values also have been used for the other temperatures, i.e. at 323 K and 373 K only the two parameters  $\Delta U_{12}$  and  $\Delta U_{21}$  remain to be determined by a best fit to the experimental data. The parameters obtained at various temperatures clearly showed their dependence on temperature. This dependence can be described by the following relations:

$$\Delta U_{12} = a_1 + b_1(1/T) \quad (14)$$

$$\Delta U_{21} = a_2 + b_2(1/T) \quad (15)$$

The constants  $a_1$ ,  $b_1$ ,  $a_2$  and  $b_2$  are different for each mixture and are all given in Table 5.

TABLE 5. Temperature independent constants to describe the temperature dependence of the MUNIQUAC-RAS interaction parameters given by eqns. (14) and (15)

| System                                      | $a_1$   | $b_1$ | $a_2$  | $b_2$  |
|---|---------|-------|--------|--------|
| 2-methoxyethanol+n-hexane                   | -2579.9 | 599.2 | 2219.6 | 35.8   |
| 2-methoxyethanol+n-heptane                  | -2684.1 | 609.8 | 3198.5 | -239.0 |
| 2-methoxyethanol+n-octane                   | -2835.0 | 650.0 | 3490.0 | -300.0 |
| 2-methoxyethanol+n-decane                   | -3050.0 | 700.0 | 4560.0 | -600.0 |
| 2-methoxyethanol+<br>2,2,4-trimethylpentane | -3281.6 | 770.7 | 5039.8 | -821.9 |

As an example in Fig. 5 it is shown for mixtures with n-hexane how well the MUNIQUAC-RAS model describes the mole fraction dependence of  $H^E$  at various temperatures. The deviation between calculated and experimental  $H^E$ -values is in the entire mole fraction range within the experimental inaccuracy. For all other mixtures the agreement is just as good.



$$\Delta U_{12} = c_1 + d_1 n \quad (16)$$

$$\Delta U_{21} = c_2 + d_1 n \quad (17)$$

The constants  $c_1$ ,  $d_1$ ,  $c_2$  and  $d_2$  consequently are depending on temperature and are given in Table 6.

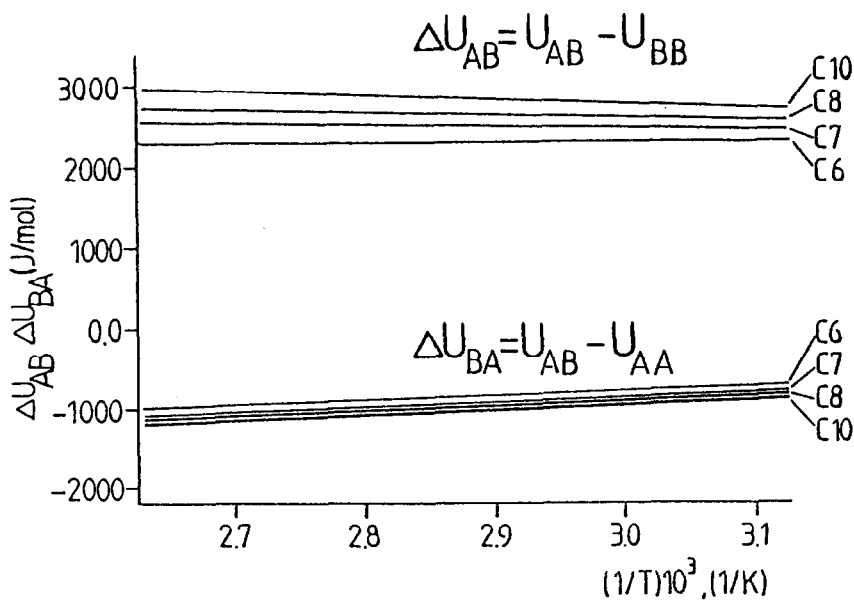


Fig. 6. Dependence of  $\Delta U_{12} \equiv \Delta U_{AB}$  and  $\Delta U_{21} \equiv \Delta U_{BA}$  on temperature for 2-methoxy-ethanol+n-alkane mixtures.

TABLE 6. Parameters for the correlation of the MUNIQUAC-RAS-parameters with the number of C-atoms of the n-alkanes according to eqns. (16) and (17).

| Temperature (K) | $c_1$  | $d_1$ | $c_2$  | $d_2$ |
|-----------------|--------|-------|--------|-------|
| 322             | -515.2 | -37.2 | 1807.8 | 90.8  |
| 345             | -602.5 | -42.5 | 1631.7 | 120.7 |
| 370             | -689.8 | -47.8 | 1455.5 | 150.5 |

Fig. 7 shows how well the linear relation between  $\Delta U_{12} \equiv \Delta U_{AB}$  and  $\Delta U_{21} \equiv \Delta U_B$  and  $n$  as given by eqns. (16) and (17) is realized.

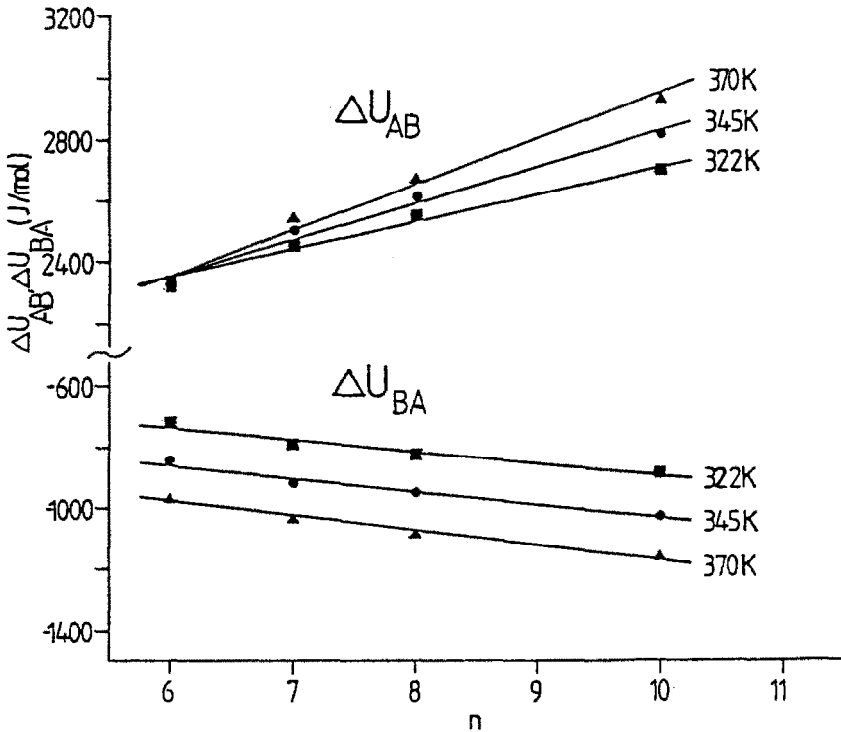


Fig. 7. Correlation of the MUNIQUAC-RAS-parameters and the number of the C-atom of the  $n$ -alkanes according to eqns. (16) and (17).

As  $K_1^0$  and  $\Delta h_1^*$  have always the same values the correlations with temperature and chain length of the  $n$ -alkane developed allow the determination of  $\Delta U_{12}$  and  $\Delta U_{21}$  by interpolation and to some extent by extrapolation to other 2-methoxyethanol- $n$ -alkane mixtures and other temperatures than covered in this work. In other words the model can be used within some border lines to precalculate  $H^E$ . The degree of branching could not be included as a correlation parameter because only one mixture containing a branched alkane has been investigated so far.

The calculations with the MUNIQUAC-RAS model clearly show that the physical contribution given by eqn. (8) is much smaller than the chemical one given by eqn. (9). As an example in Fig. 8  $H_{phys}^E$  and  $H_{chem}^E$  are compared with  $H^E$  for 2-methoxyethanol+ $n$ -hexane at 373 K and 25 bar. Only for large mole fractions of 2-methoxyethanol the physical contribution is about as large as the chemical one. H-bon-

ding accounts for the main contribution to  $H^E$  as to be expected for the type of mixtures investigated and as already discussed elsewhere (ref. 10).

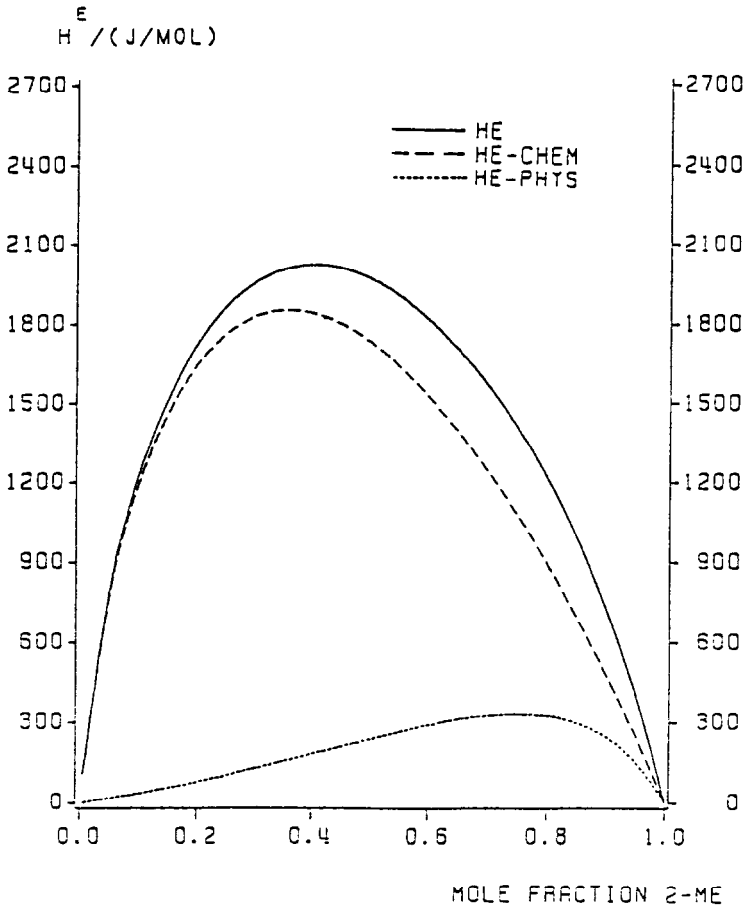


Fig. 8. Comparison of  $H^E_{phys}$  and  $H^E_{chem}$  with  $H^E = H^E_{phys} + H^E_{chem}$  for  $x$  2-methoxyethanol +  $(1-x)$  n-hexane at 373.15 K and 25 bar.

The temperature dependence of  $H^E$  also is dominated by the corresponding dependence of  $H^E_{chem}$ . In Fig. 9 the effect of temperature on  $H^E_{phys}$  and  $H^E_{chem}$  is shown again for the mixture with n-hexane. Whereas the anyhow small  $H^E_{phys}$  decreases with increasing temperature the dominating  $H^E_{chem}$  increases and determines the overall dependence on temperature. Similar behaviour is to be found for all the other mixtures investigated and confirms the dominating influence of H-bonding of  $H^E$  for mixtures containing at least one associating component.

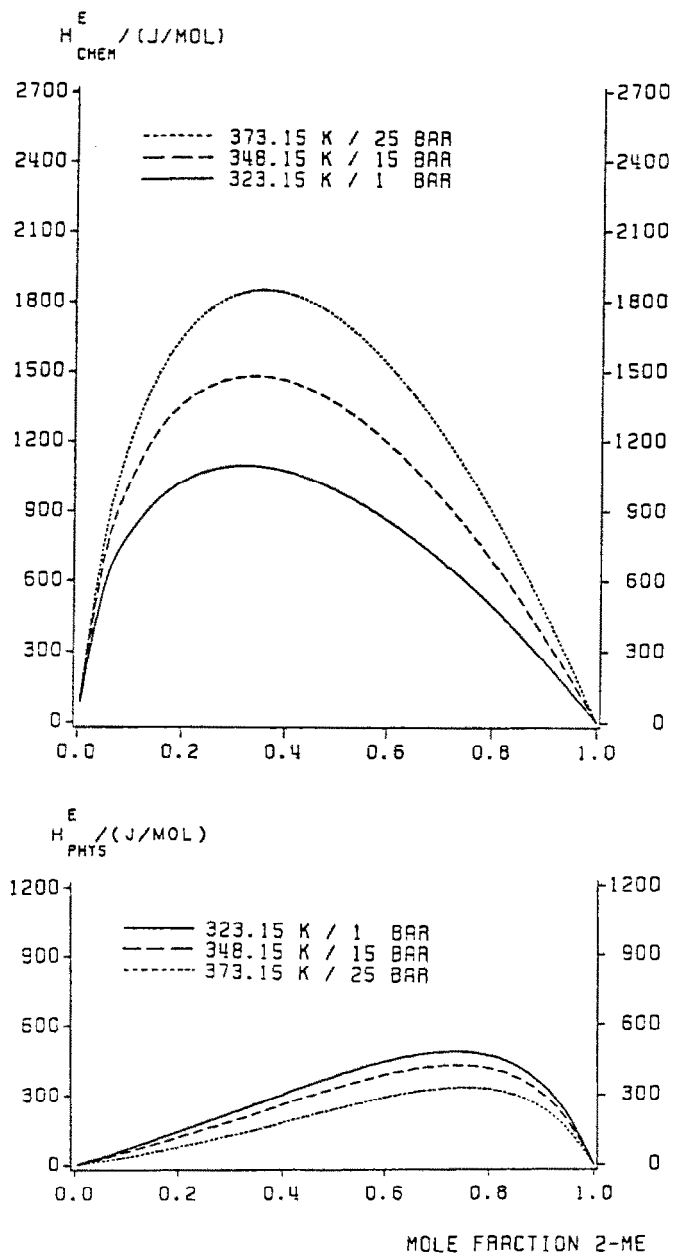


Fig. 9. Effect of temperature on  $H_{phys}^E$  and  $H_{chem}^E$  for  $x$  2-methoxyethanol +  $(1-x)$  n-hexane as calculated with eqns. (8) and (9) with parameters obtained from the correlation developed.

## CONCLUSION

The experimental results of  $H^E$  for 2-methoxyethanol+alkane mixtures show at a given temperature significant dependence on the size and shape of the alkane molecule whereas the dependence on temperature is dominated by H-bonding of 2-methoxyethanol. The concept of combining the MUNIQUAC-model for the physical contribution to  $H^E$  with the RAS-model for the chemical one leads to an expression for  $H^E$  containing four system-specific parameters. The dependence of  $H^E$  on temperature and composition can be represented very well with this model-equation. The system-specific parameters could be correlated with respect to their dependence on temperature and chain length of the n-alkane mixed with 2-methoxyethanol. Within the state conditions the correlation covers it is possible to precalculate  $H^E$  at any desired temperature and for related mixtures.

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