*Thermochimica Acta*, 19 (1977) 153–160


# THE THERMODYNAMIC PROPERTIES OF ACETALS+HEPTANE MIXTURES AT 298.15 K

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(Received 13 July 1976)

## ABSTRACT

Excess enthalpies and excess volumes were determined at 298.15 K for: dimethoxymethane+heptane, diethoxymethane+heptane, 1,1-dimethoxyethane+heptane, 1,1-diethoxyethane+heptane, 2,2-dimethoxypropane+heptane and 1,1-diethoxypropane+heptane.

## INTRODUCTION

This paper reports part of a general programme on measurements of excess volumes $V^E$, excess enthalpies $H^E$ for solutions of acetals[1,2] with different non-polar or polar solvents.

Since no thermodynamic measurements exist for mixture of acetals with heptane we have chosen in a first step to measure the enthalpies and the volumes of mixing of these binary systems.

## EXPERIMENTAL

The excess enthalpies were measured with an isothermal flow microcalorimeter Picker (Sétaram France). Details of the apparatus and procedure have been described earlier[2-5]. To check the performance of the calorimeter the heat of mixing of some binary standard systems was studied at 298.15 K. The systems used were: cyclohexane+hexane, carbon tetrachloride+benzene and benzene+cyclohexane (Table 1).

Excess volumes, $V^E$, were calculated from densities of mixtures for the entire range of composition. The densities were determined by means of an automatic digital densitometer Anton Parr. The operation of the densitometer has been described previously[9,10]. Before each measurement the densitometer was calibrated with some reference sample. The densities of pure components agreed in a number of cases with the literature values to better than $5 \cdot 10^{-5}$ g cm$^{-3}$.

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TABLE 1

EXCESS ENTHALPY $H^E$ OF STANDARD SYSTEMS AT 298.15 K

| $x_1$ | $H^E$ (J mol$^{-1}$) | $x_1$ | $H^E$ (J mol$^{-1}$) |
|---|---|---|---|
| *Cyclohexane (1)+Hexane (2)* | | | |
| 0.32612 | 166.1 | 0.69735 | 210.6 |
| 0.34439 | 175.2 | 0.71281 | 207.2 |
| 0.36253 | 180.8 | 0.72816 | 202.2 |
| 0.38052 | 186.4 | 0.7430 | 197.3 |
| 0.39837 | 193.0 | 0.75853 | 191.9 |
| 0.41608 | 199.1 | 0.77355 | 186 |
| 0.45109 | 208.2 | 0.78846 | 178 |
| 0.46839 | 211.9 | 0.80327 | 170.2 |
| 0.5026 | 218 | 0.83257 | 152.5 |
| 0.51951 | 220 | 0.84706 | 143.8 |
| 0.5363 | 221.3 | 0.86145 | 133.1 |
| 0.55294 | 221.6 | 0.87574 | 123 |
| 0.56947 | 221.8 | 0.88993 | 112 |
| 0.58588 | 222.1 | 0.90403 | 101.4 |
| 0.60216 | 222.4 | 0.91802 | 89 |
| 0.61832 | 221.5 | 0.93192 | 76.2 |
| 0.63436 | 220.7 | | |
| 0.65028 | 219.4 | | |
| 0.66609 | 216.4 | | |
| 0.68178 | 214 | | |
| *Carbon tetrachloride (1)+benzene (2)* | | | |
| 0.23432 | 88 | 0.49897 | 113.5 |
| 0.26923 | 95.4 | 0.51685 | 112.8 |
| 0.28672 | 99.7 | 0.53476 | 111.9 |
| 0.30425 | 102.3 | 0.5527 | 110.4 |
| 0.32883 | 106 | 0.57067 | 108.9 |
| 0.34643 | 108.3 | 0.58867 | 107 |
| 0.37464 | 111 | 0.6067 | 105.4 |
| 0.39231 | 112 | 0.62476 | 103.4 |
| 0.410 | 113.3 | 0.64286 | 100.8 |
| 0.42774 | 113.8 | 0.66098 | 97.8 |
| 0.44551 | 114 | 0.67913 | 94.7 |
| 0.4633 | 114.4 | 0.69732 | 91.6 |
| 0.48112 | 114 | 0.73378 | 84.3 |
| *Benzene (1)+cyclohexane (2)* | | | |
| 0.19239 | 476.5 | 0.55874 | 779 |
| 0.21298 | 514 | 0.57557 | 774.5 |
| 0.25189 | 583 | 0.59227 | 766.5 |
| 0.32783 | 680.8 | 0.60884 | 758.8 |
| 0.34644 | 704.3 | 0.62529 | 747.7 |
| 0.38322 | 733.5 | 0.64161 | 738.4 |
| 0.40139 | 748 | 0.65782 | 722.6 |
| 0.41942 | 757 | 0.6739 | 710 |
| 0.43731 | 767 | 0.68987 | 693 |
| 0.45506 | 773.3 | 0.72146 | 654 |
| 0.49015 | 781.8 | 0.73708 | 632.6 |
| 0.50058 | 782.5 | 0.79844 | 532 |
| 0.5075 | 784.7 | 0.82846 | 474 |
| 0.52471 | 785 | 0.88725 | 335 |
| 0.54179 | 782 | | |

The apparatus was tested by measuring the standard system: cyclohexane+benzene at 298.15 K. The values of $V^E$ (Table 2) agree reasonably well with the results reported in the recent works[11–14].

TABLE 2

VALUES OF THE LEAST SQUARES PARAMETERS IN EQN (1)

| *Mixture* | $A_1$ | $A_2$ | $A_3$ | $\sigma(mol^{-1})$ |
|---|---|---|---|---|
| *A. Volume of mixing $V^E$* | | | | |
| Benzene+cyclohexane | 2614.5 | −121 | − 64 | 3 |
| Dimethoxymethane+heptane | 4868 | 536 | 819 | 6 |
| Diethoxymethane+heptane | 3164 | 117 | −112 | 7 |
| 1,1-Dimethoxyethane+heptane | 4883 | − 84 | −248 | 28 |
| 1,1-Diethoxyethane+heptane | 2740 | 645 | 1547 | 17 |
| 2,2-Dimethoxypropane+heptane | 2940 | 161 | 364 | 3.8 |
| 1,1-Diethoxypropane+heptane | 1704 | −187 | | 3 |
| *B. Excess enthalpy $H^E$* | | | | |
| Cyclohexane+hexane | 864.6 | 306.7 | 77 | 0.8 |
| Carbon tetrachloride+benzene | 454.8 | − 63 | 20 | 0.3 |
| Benzene+cyclohexane | 3139.5 | 194 | 132 | 1.7 |
| Dimethoxymethane+heptane | 4031.5 | 601 | −479 | 6 |
| Diethoxymethane+heptane | 2417 | − 52 | 17 | 1.7 |
| 1,1-Dimethoxyethane+heptane | 3954 | 88 | 55 | 3.9 |
| 2,2-Dimethoxypropane+heptane | 2412 | 313 | 109 | 2.7 |
| 1,1-Diethoxypropane+heptane | 1643 | −169 | 69 | 1.9 |

*Samples*

The main impurities in commercial acetals (Fluka) are alcohols, we have purified them by fractional distillation over sodium. The other compounds hexane, heptane, cyclohexane and benzene (Merck spectrophotometric quality) have been purified chemically then fractionated twice.

Gas chromatography showed that all material was at least 99.5 moles per cent pure.

## RESULTS AND DISCUSSION

When the composition range studied was sufficiently large the measurements were fitted by a least square method in the equation

$$X^E = x_1(1-x_1)\sum_{i=1}^{n} A_i(1-2x_1)^{i-1} \qquad (1)$$

(the quantity fitted was $X^E/x_1\,(1-x_1)$ not $X^E$)

Where $x_1$ represents the mole fraction of the first named compound in the tables and $X^E$ is $H^E/(J\,mol^{-1})$ or $V^E/(10^{-9}\,m^3\,mol^{-1})$.

The parameters $A_i$ and the standard deviation $\sigma$ defined by:

$$\sigma = (\sum (H^E_{exp} - H^E_{calc})^2 / m - n)^{1/2} ,$$

where $m$ = number of measurements, $n$ = number of parameters in eqn (1) are given in Table 2. Generally it was found that three parameters were sufficient to reproduce the experimental values. The standard deviations were comparable with the estimated precision of the two apparatus.

We shall not try to give a detailed interpretation of these results until we have completed the study of binary mixtures of acetals with polar solvents. The experimental values of $V^E$ and $H^E$ are given in Tables 3 and 4.

TABLE 3

EXCESS VOLUMES $V^E$ OF ACETALS (1)+HEPTANE (2) AT 298.15 K

| $x_1$ | $V^E/10^{-9}$ ($m^3$ $mol^{-1}$) |
|---|---|
| *Dimethoxymethane + heptane* | |
| 0.2309 | 851 |
| 0.2745 | 952 |
| 0.3009 | 1011 |
| 0.3965 | 1153 |
| 0.4638 | 1201 |
| 0.4641 | 1204 |
| 0.5728 | 1218 |
| 0.6228 | 1187 |
| 0.658 | 1153 |
| 0.7375 | 1022 |
| 0.8096 | 849 |
| 0.8408 | 741 |
| 0.8877 | 571 |
| 0.8943 | 560 |
| *Diethoxymethane + heptane* | |
| 0.1997 | 483 |
| 0.3525 | 725 |
| 0.3954 | 756 |
| 0.4908 | 791 |
| 0.4931 | 790 |
| 0.5464 | 779 |
| 0.5668 | 778 |
| 0.56755 | 776 |
| 0.5975 | 760 |
| 0.6132 | 752 |
| 0.7124 | 663 |
| *1,1-Dimethoxyethane + heptane* | |
| 0.1752 | 675 |
| 0.1914 | 741 |
| 0.2162 | 854 |
| 0.3807 | 1197 |
| 0.47515 | 1196 |

TABLE 3 *(continued)*

| $x_1$ | $V^E/10^{-9}$ ($m^3$ $mol^{-1}$) |
|---|---|
| 0.53015 | 1196 |
| 0.8926 | 436.5 |
| 0.9197 | 346.5 |
| 0.9350 | 285 |
| *1,1-Diethoxyethane + heptane* | |
| 0.15215 | 372 |
| 0.2261 | 505 |
| 0.2632 | 542 |
| 0.3025 | 596 |
| 0.3484 | 630 |
| 0.4251 | 660 |
| 0.6440 | 706 |
| 0.7213 | 647 |
| 0.7713 | 611 |
| 0.8352 | 525 |
| 0.84535 | 499 |
| 0.9194 | 340 |
| *2,2-Dimethoxypropane + heptane* | |
| 0.1919 | 461 |
| 0.3217 | 643 |
| 0.4075 | 702 |
| 0.4793 | 729 |
| 0.4903 | 734 |
| 0.6136 | 715 |
| 0.6668 | 677 |
| 0.7051 | 636 |
| 0.76525 | 558 |
| 0.8573 | 398 |
| *1,1-Diethoxypropane + heptane* | |
| 0.05305 | 95 |
| 0.1267 | 210 |
| 0.1746 | 268.5 |
| 0.2936 | 378 |
| 0.4711 | 435.5 |
| 0.6090 | 398 |
| 0.6479 | 388 |
| 0.6591 | 377 |
| 0.7336 | 326 |
| 0.8435 | 212 |
| 0.91335 | 126 |

TABLE 4

EXCESS ENTHALPY $H^E$ OF ACETALS (1)+HEPTANE AT 298.15 K

| $x_1$ | $H^E$ (J mol$^{-1}$) | $x_1$ | $H^E$ (J mol$^{-1}$) |
|---|---|---|---|
| *Dimethoxymethane + heptane* | | | |
| 0.34595 | 857 | 0.6256 | 967 |
| 0.36725 | 885 | 0.6416 | 957 |
| 0.3881 | 914 | 0.6573 | 933 |
| 0.40857 | 946 | 0.6880 | 892 |
| 0.4483 | 986 | 0.7029 | 869 |
| 0.46755 | 1000 | 0.7176 | 846 |
| 0.4865 | 1013 | 0.7320 | 826 |
| 0.5050 | 1015 | 0.7462 | 801 |
| 0.5232 | 1017 | 0.7602 | 775 |
| 0.5411 | 1016 | 0.7739 | 744 |
| 0.5586 | 1014 | 0.7874 | 717 |
| 0.5758 | 1004 | | |
| 0.5927 | 993 | | |
| 0.6093 | 981 | | |
| *Diethoxymethane + heptane* | | | |
| 0.13051 | 281.4 | 0.53586 | 603.4 |
| 0.20901 | 405.5 | 0.55285 | 598.0 |
| 0.24741 | 455.0 | 0.56972 | 592.6 |
| 0.28527 | 497.0 | 0.58648 | 584 |
| 0.32259 | 531.0 | 0.60313 | 575 |
| 0.35938 | 559.6 | 0.6361 | 557 |
| 0.39566 | 578.5 | 0.66863 | 533.0 |
| 0.43144 | 592 | 0.70074 | 504.0 |
| 0.44914 | 596.6 | 0.76369 | 434.0 |
| 0.48419 | 603.6 | 0.79456 | 389 |
| 0.50153 | 605.0 | 0.82504 | 343.5 |
| 0.51875 | 605.5 | | |
| *1,1-Dimethoxyethane + heptane* | | | |
| 0.22293 | 675.0 | 0.5333 | 986.0 |
| 0.26557 | 768.0 | 0.54373 | 983.7 |
| 0.34733 | 894.0 | 0.56769 | 977 |
| 0.38654 | 941.0 | 0.6012 | 956.0 |
| 0.42471 | 967.0 | 0.63387 | 922.0 |
| 0.46187 | 978.0 | 0.66575 | 884.0 |
| 0.48009 | 981.0 | 0.72721 | 792.0 |
| 0.49806 | 984.0 | 0.78582 | 681.5 |
| 0.51581 | 986.0 | 0.8141 | 609.5 |
| *2,2-Dimethoxypropane + heptane* | | | |
| 0.20609 | 367 | 0.53767 | 603 |
| 0.22578 | 393 | 0.55477 | 602 |
| 0.2453 | 419.0 | 0.57174 | 600 |
| 0.26469 | 444.5 | 0.58858 | 597 |
| 0.2839 | 470 | 0.60530 | 592.7 |
| 0.30297 | 489.5 | 0.62189 | 586 |
| 0.32189 | 509 | 0.63836 | 576.6 |
| 0.34065 | 525 | 0.6547 | 568 |
| 0.35927 | 540 | 0.67094 | 556.4 |

TABLE 4 *(continued)*

| $x_1$ | $H^E$ (J mol$^{-1}$) | $x_1$ | $H^E$ (J mol$^{-1}$) |
|---|---|---|---|
| 0.37774 | 553.6 | 0.68705 | 546.0 |
| 0.39607 | 568 | 0.70304 | 531 |
| 0.41425 | 576.6 | 0.7189 | 517.4 |
| 0.43229 | 585 | 0.73468 | 502 |
| 0.45019 | 591 | 0.7503 | 486.0 |
| 0.46796 | 596.0 | 0.76585 | 468.0 |
| 0.48559 | 600.6 | 0.78128 | 450.0 |
| 0.50308 | 602 | 0.79659 | 431 |
| 0.52044 | 603 | 0.81179 | 408 |
| *1,1-Diethoxypropane+heptane* | | | |
| 0.12499 | 200 | 0.49837 | 412 |
| 0.15822 | 238.7 | 0.51576 | 411 |
| 0.19159 | 275.6 | 0.53319 | 408.4 |
| 0.2251 | 305.0 | 0.55066 | 404 |
| 0.25875 | 332.0 | 0.56817 | 400.3 |
| 0.29254 | 355.0 | 0.58571 | 393 |
| 0.32648 | 373.7 | 0.60329 | 385.9 |
| 0.36056 | 390.5 | 0.62091 | 378.7 |
| 0.37766 | 396 | 0.63857 | 371.4 |
| 0.39479 | 399.5 | 0.65627 | 362.5 |
| 0.41196 | 403.5 | 0.67401 | 352.5 |
| 0.42917 | 406.5 | 0.69178 | 340 |
| 0.44641 | 410.5 | 0.70959 | 327 |
| 0.4637 | 411.4 | 0.74534 | 299.3 |
| 0.48101 | 411.8 | 0.78124 | 263.7 |

The excess thermodynamic properties are large and positive and almost symmetrical about $x_1 = 1-x_1$. The effect of molecular size on the excess properties of mixing may be judged from Tables 3 and 4. $X^E$ decreases as the molar volume of the acetal increases. Isomeric acetals with similar molar volumes c.a. diethoxymethane and 2,2-dimethoxypropane have almost identical heats and excess volumes of mixing.

The enthalpies of mixing of the 1,1-diethoxyethane+heptane system has not yet been studied but the values can be evaluated by the generalized form of lattice theory of mixtures developed by Kehiaian et al.[15]. For $x_1 = 1-x_1$ $H^E_{cal} = 510$ J mol$^{-1}$. The values of the system dimethoxymethane+heptane was used to establish a consistent value of an interchange enthalpy $h^*_{ac}$ of the oxygen acetal with aliphatic segments. The interchange enthalpy obtained in this way ($h^*_{ac} = 6070 \pm 250$ J mol$^{-1}$) is consistent with the parameters reported recently for example:

| | |
|---|---|
| aliphatic/etheric[15] | $h^*_{ac} = 9950 \pm 50$ J mol$^{-1}$ |
| aliphatic/amine[16] | $h^*_{ac} = 15062 \pm 700$ J mol$^{-1}$ |
| aliphatic/nitroalkane[17] | $h^*_{ac} = 5648 \pm 272$ J mol$^{-1}$ |

A systematic study will be presented when the experimental work has been completed.

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