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# Enthalpies of solution of aliphatic compounds in dimethyl sulfoxide

Takayoshi Kimura*, Takanori Matsushita, Tadashi Kamiyama

*Department of Chemistry, Faculty of Science and Technology, Kinki University, Kowakae, Higashi-Osaka 577-8502, Japan*

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**Abstract**

Enthalpies of solution of aliphatic alcohols $\{CH_3(CH_2)_nOH, n = 0\text{–}10\}$ and aliphatic nitriles $\{CH_3(CH_2)_nCN, n = 0\text{–}12\}$ in dimethyl sulfoxide (DMSO) have been determined at 298.15 K for the mole fraction range $5 \times 10^{-5}$ to 0.002. In all cases enthalpies of solution were found to be positive. Partial molar enthalpies of solution at infinite dilution were derived.

Linear relations between the limiting excess partial molar enthalpies and the number of methylene groups were found for both groups of compounds investigated. McMillan–Mayer's parameters, $h_{xx}$ and $h_{xxx}$, showed unfavorable and favorable interactions, respectively.

*Keywords:* Enthalpies; DMSO; Aliphatic nitriles; Aliphatic alcohols

## 1. Introduction

In our previous papers [1–13], excess thermodynamic functions were reported for the binary mixtures of dimethyl sulfoxide (DMSO) with water, benzene, [1,2], methyl methylthiomethyl sulfoxide (MMTSO), carbon tetrachloride, chloroform, dichloromethane [3], deuterochloroform [4], alkane-1-ols $\{CH_3(CH_2)_nOH, n = 1\text{–}9\}$ [5], methylbenzenes $\{C_6H_{6-m}(CH_3)_m, m = 1, 2, 3\}$ [6], cycloethers [7], alkyl ethers [8], benzene derivatives [9–11], halogenated aromatic compounds [12,13] and those of MMTSO.

In the present paper, results of microcalorimetric measurements of enthalpies of solution of aliphatic alcohols (ROH) and nitriles (RCN) in DMSO, at 298.15 K in the mole fraction range $x = 5 \times 10^{-5}$ to 0.002. The calorimetric measurements were supported by determination of densities. Correlations were made with the molecular structures of ROH and RCN. Virial coefficients of the McMillan-Meyer equation were derived and were briefly discussed.

## 2. Experimental

### 2.1. Materials and methods

DMSO (Cica-Merck, uvasol) was purified and the final purity was the same as those described previously [1,2]. The alcohols $\{CH_3(CH_2)_nOH, n = 0\text{–}10\}$ and the nitriles $\{CH_3(CH_2)_nCN, n = 0\text{–}12\}$ (Kishida Chemical, Special grade) were fractionally distilled over freshly activated molecular sieves of 4 Å which had been evacuated at 453 K for 12 h under $10^{-2}$ to $10^{-3}$ Pa. GLC analysis (2 m columns with 10% SE-30 on chromosorb and 20% PEG-1000 on celite 545 with FID on Yanagimoto G180FP) showed only trace impurity peaks (<0.1 ppm). Coulometric Karl–Fischer's method using a Moisturemeter (Mitsubishi Chemical Ind., CA-02) showed that the water content of all samples was 0.01 mol% or less.

A twin titration microcalorimeter of the heat-conduction type, Thermal Activity Monitor (Thermometric AB, Järfälla, Sweden) fitted with a large reaction vessel, volume 20 cm$^3$, was used for the measurements of enthalpies of solution at 298.15 K. Details of the calorimetric procedure have been described previously [14,15]. Samples (2.5 μl) were injected into the vessel by use of gas-tight syringes (Hamilton 1710 N or 1725 N) fitted with stain less-steel needles (i.d.: 0.2 mm, o.d.: 0.45 mm, length: 1 m). Final mole fractions were in the

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* Corresponding author. Tel.: +81-6-721-2332x4112; fax: +81-6-723-2721.

*E-mail address:* kimura@chem.kindai.ac.jp (T. Kimura).

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range of $x = 5 \times 10^{-5}$ to 0.002. The amounts of ROH and RCN injected into the calorimetric vessel were calculated by volume. The syringes, charged with different volumes of water, were calibrated by weighing (Mettler microbalance ME30). Regression curves were prepared for each syringe.

Accurate values for the densities of the compounds were needed for the syringe injections. Measurements were conducted at (298.15 ± 0.001) K by use of a vibrating-tube densitometer (Anton Paar DMA55).

The solution of propane-1-ol in water was used as a test reaction [16] for the calorimetric measurements. The test experiments were conducted under conditions closely similar to those of the solution experiments with ROH and RCN in DMSO. Enthalpies of solution of the alcohols and the nitriles were measured by 10 or more consecutive injections into DMSO.

## 3. Results and discussion

Results of the propane-1-ol test experiments are summarized in Fig. 1. Using a least squares procedure, Eq. (1) was derived:

$$\Delta_{sol} H = -10.14 + 25.79x \tag{1}$$

where $x$ is mole fraction of propane-1-ol. Smoothed values calculated from Eq. (1) are shown in Fig. 1 and the enthalpy value at infinite dilution was found to be $\Delta_{sol} H^{\infty} = (-10.12 \pm 0.02)\,\mathrm{kJ\,mol^{-1}}$, in agreement with the value recommended by IUPAC [16], $\Delta_{sol} H^{\infty} = (-10.16 \pm 0.02)\,\mathrm{kJ\,mol^{-1}}$ in Table 1 (Fig. 2).

Results of density measurements are listed in Table 2. The values agree with the reference values shown in the 4th and the 7th columns of Table 2.

Table 1
Enthalpies of solution of propane-1-ol in water at infinite dilution at 298.15 K

| $\Delta_{soln} H^{\infty}$ (kJ mol$^{-1}$) | Reference |
|---|---|
| −10.14 ± 0.02 | This work |
| −10.16 ± 0.02 | IUPAC [16] |
| −10.16 ± 0.02 | [17] |
| −10.16 ± 0.02 | [18] |
| −10.13 ± 0.26 | [19] |

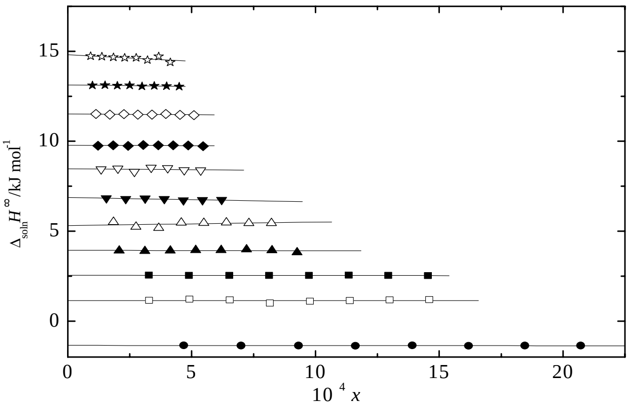

Fig. 2. Examples of enthalpies of solution of $x\mathrm{CH_3(CH_2)}_n\mathrm{OH}$ ($n$ = 0–10) + (1 − $x$)DMSO at 298.15 K. (●) $n$ = 0, (☐) $n$ = 1, (■) $n$ = 2, (▲) $n$ = 3, (△) $n$ = 4, (▼) $n$ = 5, (▽) $n$ = 6, (◆) $n$ = 7, (◇) $n$ = 8, (★) $n$ = 9, (☆) $n$ = 10.

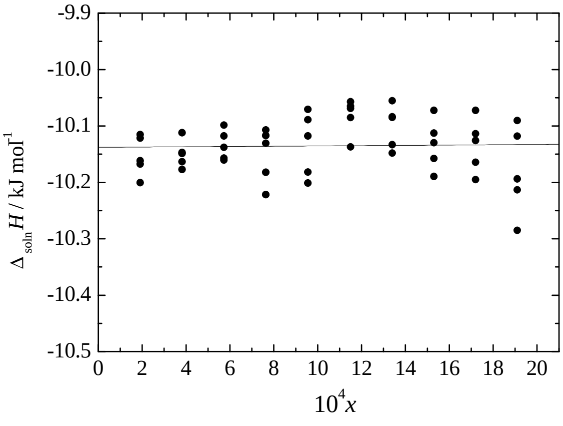

Fig. 1. Enthalpies of solution of (1 − $x$)water + $x$propane-1-ol in water at 298.15 K: $\Delta_{soln} H$ (kJ mol$^{-1}$) = −10.14 + 25.79$x$, $s_f$ = 0.02 kJ mol$^{-1}$.

Results of the solution measurements of alcohols and nitriles in DMSO are listed in Table 3 and shown in Figs. 2 and 3. The enthalpies of solution are fitted to the linear equation (2) by least squares treatment. Values for the coefficients $a$ and $b$ and the standard deviations are summarized in Table 3

$$\Delta_{sol} H = a + bx \tag{2}$$

Coefficient $a$ in Eq. (2) corresponds to enthalpy of solution at infinite dilution, $\Delta_{sol} H^{\infty}$, whereas $b$ is related to solute–solute interactions.

$\Delta_{sol} H^{\infty}$ values were fitted to Eq. (3) by a method of least squares:

$$\Delta_{sol} H^{\infty} = a + b(n+1) \tag{3}$$

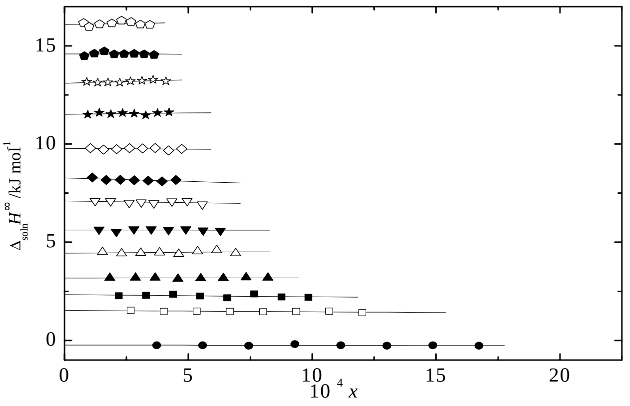

Fig. 3. Examples of enthalpies of solution of $x\mathrm{CH_3(CH_2)}_n\mathrm{CN}$ ($n$ = 0–12) + (1 − $x$)DMSO at 298.15 K. (●) $n$ = 0, (☐) $n$ = 1, (■) $n$ = 2, (▲) $n$ = 3, (△) $n$ = 4, (▼) $n$ = 5, (▽) $n$ = 6, (◆) $n$ = 7, (◇) $n$ = 8, (★) $n$ = 9, (☆) $n$ = 10, (⬟) $n$ = 11, (⬠) $n$ = 12.

Table 2
Densities of alkyl alcohols and nitriles used at 298.15 K in g cm$^{-3}$

| $n$ | $CH_3(CH_2)_nCN$ | | | $CH_3(CH_2)_nOH$ | | |
|---|---|---|---|---|---|---|
| | $\rho$ | $10^5$ S.D. $\rho$ | $\rho$ [Ref.] | $\rho$ | $10^5$ S.D. $\rho$ | $\rho$ [Ref.] |
| 0 | 0.77639 | 4.1 | 0.77649 [19] | 0.78653 | 3.5 | 0.78637 [22] |
| 1 | 0.77649 | 3.5 | 0.77682 [20] | 0.78508 | 2.5 | 0.78493 [22] |
| 2 | 0.78617 | 3.2 | 0.7865 [21] | 0.79952 | 3.3 | 0.79960 [22] |
| 3 | 0.79451 | 3.6 | 0.7950 [21] | 0.80591 | 2.1 | 0.80575 [22] |
| 4 | 0.80189 | 1.5 | 0.8012 [21] | 0.81076 | 3.5 | 0.81080 [22] |
| 5 | 0.80661 | 3.1 | | 0.81546 | 4.5 | 0.81534 [23] |
| 6 | 0.80926 | 5.1 | 0.8097 [21] | 0.81861 | 3.1 | 0.81875 [24] |
| 7 | 0.81412 | 3.5 | | 0.82144 | 1.6 | 0.82157 [22] |
| 8 | 0.81660 | 1.6 | | 0.82394 | 3.4 | 0.82423 [24] |
| 9 | 0.81725 | 0.92 | | 0.82569 | 3.6 | 0.82965 [22] |
| 10 | 0.82041 | 1.4 | | 0.82811 | 1.6 | |
| 11 | 0.82208 | 1.1 | | | | |
| 12 | 0.82390 | 4.1 | | | | |

where $n$ is the number of methylene groups in the molecules. A terminal group of methyl group was dealt with one methylene group and one hydrogen. The coefficients $a$ and $b$ in Eq. (3) are listed in Table 4. The linear increase of $\Delta_{\mathrm{sol}}H^{\infty}$ as a function of $n$, shown in Fig. 4 for ROH and RCN, was derived from smoothed values calculated by use of the coefficients in Table 4. Values for coefficient $a$ in Eq. (3) are negative, which implies that the contacts between DMSO and the functional groups –OH and –CN stabilize the systems. The stabilization of DMSO–ROH is 22% larger than that for DMSO–RCN. Enthalpies solution at infinite dilution increased with increasing number of methylene groups. All coefficients $b$ of ROH and RCN in Eq. (3) were positive indicating unfavorable interactions between the sulfoxide group and the alkyl groups of ROH and RCN.

The functional groups of ROH and RCN have opposite effects in their interactions with the sulfoxide group. The polar sulfoxide group might disturb favorable non-polar van der Waals interactions between alkyl groups in the pure liquids of ROH and RCN.

Excess thermodynamic properties of multi-component mixtures can be expressed by virial coefficients of the McMillan–Mayer equation (4) [25,26]. They reflect the non-ideal contributions to a thermodynamic function in terms of interaction parameters of pair, triplet and the higher orders:

$$\Delta H(m) = h_{xx}m + h_{xxx}m^2 + h_{xxxx}m^3 + \cdots \tag{4}$$

where $m$ is the molality of the solutes and $h_{xx}$, $h_{xxx}$, $h_{xxxx}$ are the enthalpic pair, triplet and quadruplet body interactions parameters, respectively. It is judged that in the concentration range studied, contributions of quadruplet and the higher order interaction terms can be neglected. The $h_{xx}$ and $h_{xxx}$ for the systems of ROH–DMSO and RCN–DMSO were determined by means of least squares, and listed in Table 5. The $h_{xx}$ values are in all cases positive, except for the first members of the series, methanol and acetonitrile. That may be interpreted as unfavorable pair-wise interactions between DMSO and the alkyl compounds. In contrast, values for the triplet body's interaction parameters are positive for the first

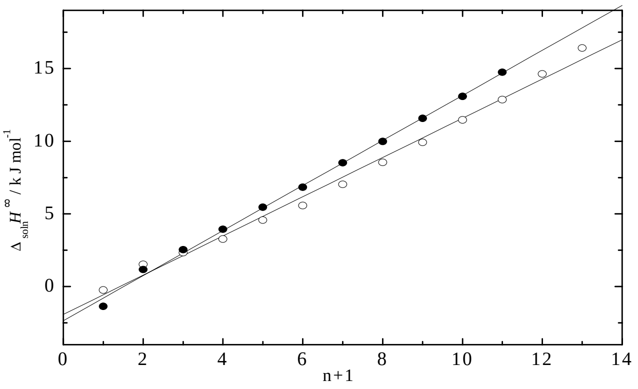

Fig. 4. Correlation between enthalpies of solution at infinite dilution and number of methylene groups of aliphatic compounds. (●) $x\mathrm{CH_3(CH_2)_nOH}$ ($n$ = 0–10) + $(1 - x)$DMSO, (○) $x\mathrm{CH_3(CH_2)_nCN}$ ($n$ = 0–12) + $(1 - x)$DMSO.

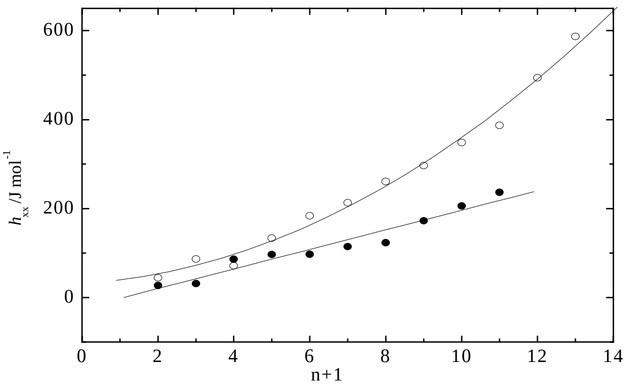

Fig. 5. Correlation between McMillan–Mayer's parameters of $h_{xx}$ and number of methylene groups of aliphatic compounds. (●) $x\mathrm{CH_3(CH_2)_nOH}$ ($n$ = 0–10) + $(1 - x)$DMSO, (○) $x\mathrm{CH_3(CH_2)_nCN}$ ($n$ = 0–12) + $(1 - x)$DMSO.

Table 3
Best-fits coefficients $a$ and $b$ in Eq. (2)

| $10^4x_i$ | $10^4x_f$ | $a$ (kJ mol$^{-1}$) | $b$ (kJ mol$^{-1}$) | $10^2$ $s_f$ (kJ mol$^{-1}$) | $10^4x_i$ | $10^4x_f$ | $a$ (kJ mol$^{-1}$) | $b$ (kJ mol$^{-1}$) | $10^2$ $s_f$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| $x\mathrm{CH_3CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = -0.2420 \pm 0.003$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)7CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 8.536 \pm 0.054$ kJ mol$^{-1}$) | | | | |
| 1.861 | 16.73 | −0.2411 | 0.050 | 1.0 | 0.5707 | 5.134 | 8.598 | −9.469 | 12 |
| 1.830 | 16.45 | −0.2403 | 0.012 | 0.6 | 0.5595 | 5.033 | 8.502 | −5.465 | 9.2 |
| 1.828 | 16.43 | −0.2458 | 0.001 | 1.6 | 0.5626 | 4.499 | 8.507 | −7.880 | 4.5 |
| $x\mathrm{CH_3(CH_2)CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 1.530 \pm 0.016$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)8CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 9.919 \pm 0.024$ kJ mol$^{-1}$) | | | | |
| 1.387 | 12.47 | 1.512 | −0.297 | 5.1 | 0.5121 | 4.607 | 9.941 | −10.16 | 7.6 |
| 1.337 | 12.02 | 1.543 | 0.847 | 2.2 | 0.5058 | 4.550 | 9.924 | −6.826 | 10 |
| 1.354 | 12.18 | 1.535 | 0.429 | 5.6 | 0.5086 | 4.576 | 9.893 | −2.155 | 4.2 |
| $x\mathrm{CH_3(CH_2)2CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 2.333 \pm 0.006$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)9CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 11.46 \pm 0.081$ kJ mol$^{-1}$) | | | | |
| 1.100 | 9.892 | 2.340 | −0.655 | 5.7 | 0.4724 | 4.250 | 11.37 | 3.765 | 10 |
| 1.097 | 9.861 | 2.328 | 1.443 | 4.4 | 0.4707 | 3.764 | 11.49 | −4.160 | 15 |
| 1.105 | 9.935 | 2.331 | 0.175 | 8.3 | 0.4692 | 4.221 | 11.52 | 1.221 | 6.1 |
| $x\mathrm{CH_3(CH_2)3CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 3.261 \pm 0.012$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)10CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 12.85 \pm 0.053$ kJ mol$^{-1}$) | | | | |
| 0.9198 | 8.272 | 3.254 | 0.017 | 7.1 | 0.4301 | 3.869 | 12.86 | 3.371 | 12 |
| 0.9164 | 8.241 | 3.275 | −0.199 | 3.0 | 0.4384 | 3.944 | 12.90 | 4.275 | 9.1 |
| 0.9188 | 8.263 | 3.255 | −0.865 | 5.9 | 0.4384 | 3.944 | 12.79 | 1.553 | 14 |
| $x\mathrm{CH_3(CH_2)4CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 4.577 \pm 0.043$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)11CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 14.62 \pm 0.038$ kJ mol$^{-1}$) | | | | |
| 0.7909 | 7.114 | 4.528 | −0.034 | 4.1 | 0.4026 | 3.622 | 14.58 | 1.072 | 7.2 |
| 0.7861 | 7.070 | 4.593 | −2.193 | 9.4 | 0.4057 | 3.650 | 14.66 | −4.945 | 8.1 |
| 0.7941 | 7.143 | 4.609 | −0.133 | 2.6 | 0.4077 | 3.668 | 14.62 | −4.454 | 11 |
| $x\mathrm{CH_3(CH_2)5CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 5.579 \pm 0.015$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)12CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 16.41 \pm 0.155$ kJ mol$^{-1}$) | | | | |
| 0.7002 | 6.298 | 5.585 | 1.480 | 5.4 | 0.3788 | 3.408 | 16.44 | −5.689 | 6.9 |
| 0.6970 | 6.269 | 5.562 | 1.321 | 13 | 0.3762 | 3.385 | 16.25 | 4.080 | 17 |
| 0.6901 | 6.207 | 5.590 | 1.334 | 11 | 0.3739 | 3.364 | 16.56 | −10.98 | 12 |
| $x\mathrm{CH_3(CH_2)6CN} + (1-x)\mathrm{DMSO}$ ($a_{av} = 7.028 \pm 0.072$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = -1.367 \pm 0.010$ kJ mol$^{-1}$) | | | | |
| 0.6368 | 5.728 | 7.076 | −0.344 | 3.9 | 2.363 | 18.60 | −1.377 | 0.115 | 0.3 |
| 0.6316 | 5.682 | 7.063 | −1.800 | 3.3 | 2.352 | 20.78 | −1.367 | 0.468 | 1.1 |
| 0.6178 | 5.557 | 6.946 | 1.030 | 0.6 | 2.344 | 20.71 | −1.357 | −0.073 | −0.2 |
| $x\mathrm{CH_3(CH_2)OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = 1.167 \pm 0.021$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)6OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = 8.510 \pm 0.024$ kJ mol$^{-1}$) | | | | |
| 1.641 | 14.58 | 1.144 | 0.332 | 0.5 | 0.6779 | 6.068 | 8.484 | −3.191 | −2.2 |
| 1.643 | 14.60 | 1.186 | −0.320 | −0.5 | 0.6744 | 6.037 | 8.530 | −4.227 | −2.9 |
| 1.634 | 14.52 | 1.172 | −0.458 | −0.7 | 0.6743 | 5.369 | 8.521 | −1.878 | −1.3 |
| $x\mathrm{CH_3(CH_2)2OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = 2.540 \pm 0.002$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)7OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = 9.980 \pm 0.059$ kJ mol$^{-1}$) | | | | |
| 1.278 | 11.38 | 2.537 | −0.381 | −0.5 | 0.6101 | 5.464 | 9.935 | 2.734 | 1.7 |
| 1.637 | 14.54 | 2.541 | −0.048 | −0.1 | 0.6084 | 5.449 | 10.05 | −2.741 | −1.7 |
| 1.640 | 12.97 | 2.541 | −0.464 | −0.8 | 0.6185 | 5.539 | 9.968 | 0.417 | 0.3 |
| $x\mathrm{CH_3(CH_2)3OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = 3.940 \pm 0.011$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)8OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = 11.57 \pm 0.029$ kJ mol$^{-1}$) | | | | |
| 1.039 | 9.273 | 3.932 | −0.510 | −0.5 | 0.5547 | 4.990 | 11.57 | −4.318 | −2.4 |
| 1.047 | 8.313 | 3.934 | −0.408 | −0.4 | 0.5566 | 5.007 | 11.54 | −4.958 | −2.8 |
| 1.055 | 9.413 | 3.953 | −0.537 | −0.6 | 0.5516 | 4.962 | 11.60 | −1.397 | −0.8 |
| $x\mathrm{CH_3(CH_2)4OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = 5.452 \pm 0.032$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)9OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = 13.08 \pm 0.046$ kJ mol$^{-1}$) | | | | |
| 0.8842 | 7.902 | 5.476 | −0.782 | −0.7 | 0.4996 | 4.494 | 13.13 | −1.612 | −0.8 |
| 0.8813 | 7.007 | 5.415 | −0.410 | −0.4 | 0.5044 | 4.538 | 13.04 | 2.721 | 1.4 |
| 0.8819 | 7.012 | 5.464 | −0.676 | −0.6 | 0.4989 | 4.488 | 13.08 | −0.252 | −0.1 |
| $x\mathrm{CH_3(CH_2)5OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = 6.829 \pm 0.038$ kJ mol$^{-1}$) | | | | | $x\mathrm{CH_3(CH_2)10OH} + (1-x)\mathrm{DMSO}$ ($a_{av} = 14.75 \pm 0.076$ kJ mol$^{-1}$) | | | | |
| 0.7674 | 6.106 | 6.787 | −1.372 | −1.1 | 0.4597 | 4.136 | 14.70 | −0.911 | −0.4 |
| 0.7811 | 6.215 | 6.860 | −2.175 | −1.7 | 0.4574 | 4.115 | 14.84 | −15.8 | −7.2 |
| 0.7632 | 6.073 | 6.840 | −2.141 | −1.6 | 0.4559 | 4.101 | 14.70 | 0.926 | 0.4 |

Table 4
Best-fits coefficients of Eq. (3)

| System | $a$ | $b$ | $R$ | $s_f$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| $\mathrm{CH_3(CH_2)}_n\mathrm{CN}$ | $-1.92 \pm 0.28$ | $1.35 \pm 0.04$ | 0.996 | 0.47 ($n$ = 0–12) |
| $\mathrm{CH_3(CH_2)}_n\mathrm{OH}$ | $-2.35 \pm 0.17$ | $1.55 \pm 0.02$ | 0.999 | 0.26 ($n$ = 0–10) |

Table 5
McMillan–Mayer's parameter $h_{xx}$ or $h_{xxx}$ of alkyl compounds at 298.15 K

| $n$ | $CH_3(CH_2)_nCN$ | | $CH_3(CH_2)_nOH$ | |
|---|---|---|---|---|
| | $h_{xx}$ (J kg$^{-1}$ mol$^{-1}$) | $h_{xxx}$ (kJ kg$^{-2}$ mol$^{-2}$) | $h_{xx}$ (J kg$^{-1}$ mol$^{-1}$) | $h_{xxx}$ (kJ kg$^{-2}$ mol$^{-2}$) |
| 0 | −10.1 | 0.245 | −52.9 | 1.87 |
| 1 | 44.4 | −1.89 | 27.2 | −0.942 |
| 2 | 86.5 | −5.11 | 31.7 | −1.52 |
| 3 | 71.5 | −6.23 | 86.1 | −6.22 |
| 4 | 134 | −11.9 | 97.0 | −7.32 |
| 5 | 184 | −14.1 | 97.3 | −8.57 |
| 6 | 213 | −16.5 | 115 | −9.70 |
| 7 | 261 | −19.5 | 123 | −11.5 |
| 8 | 297 | −33.7 | 173 | −17.5 |
| 9 | 349 | −43.6 | 206 | −22.7 |
| 10 | 387 | −50.6 | 236 | −22.7 |
| 11 | 494 | −64.0 | | |
| 12 | 587 | −83.9 | | |

Table 6
Coefficients of Eq. (5)

| | $A_1$ (kJ mol$^{-1}$) | $A_2$ (kJ mol$^{-1}$ $n^{-1}$) | $A_3$ (kJ mol$^{-1}$ $n^{-2}$) | $s_f$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| $CH_3(CH_2)_nCN$ ($n = 0$–$12$) | | | | |
| $h_{xx}$ | −0.090 | 0.0465 | | 0.037 |
| $h_{xxx}$ | −10.0 | 4.0 | −0.73 | 3.0 |
| $CH_3(CH_2)_nOH$ ($n = 0$–$10$) | | | | |
| $h_{xx}$ | −0.024 | 0.022 | | 0.017 |
| $h_{xxx}$ | 5.44 | −2.51 | | 2.0 |

members, but are negative for the higher members of the series.

In order to further illustrate the effect of the length of the alkyl chains, the $h_{xx}$ and $h_{xxx}$ were fitted by a least squares treatment to Eq. (5)

$$h_{xx} \text{ or } h_{xxx} = A_1 + A_2(n+1) + A_3(n+1)^2 \qquad (5)$$

Values for the coefficients $A_1$, $A_2$ and $A_3$ are summarized in Table 6. In Figs. 5 and 6 values for the interaction parameters $h_{xx}$ and $h_{xxx}$, respectively, are plotted against $n$. Fig. 5 shows that for the alcohols $h_{xx}$ values increase linearly with increasing number of methylene groups. For the nitriles corresponding deviation is non-linear and is more pronounced. Corresponding variation of the $h_{xxx}$ values (Fig. 6) is again linear for the alcohols, but decreases with increasing $n$. For the nitriles the $h_{xxx}$ values decrease more rapidly and in a non-linear mode.

In order to reach a better understanding of the effect of hydroxyl and nitrile groups on the McMillan–Mayer parameters, enthalpies of solution in DMSO of other

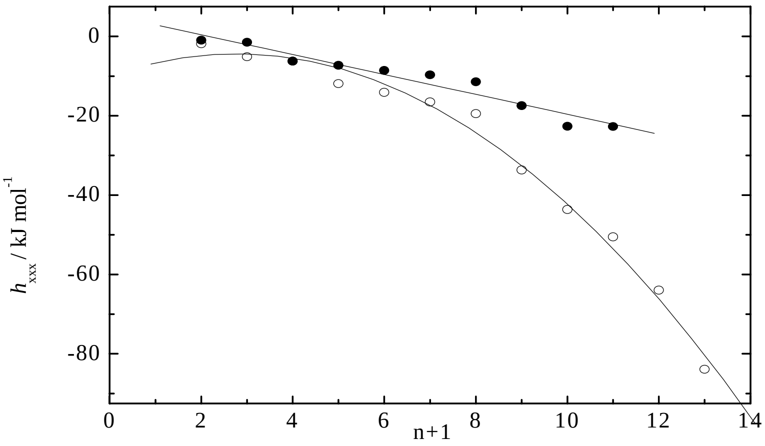

Fig. 6. Correlation between McMillan–Mayer's parameters of $h_{xxx}$ and number of methylene groups of aliphatic compounds. (●) $xCH_3(CH_2)_nOH$ ($n = 0$–$11$) + $(1 - x)$DMSO, (○) $xCH_3(CH_2)_nCN$ ($n = 0$–$12$) + $(1 - x)$DMSO.

series of alkyl compounds are presently being studied by solution calorimetry. Results will be reported in the near future.

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