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Excess molar enthalpies and heat capacities of dimethyl sulfoxide + seven normal alkanols at 303.15 K and atmospheric pressure

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Abstract

Excess molar enthalpies and heat capacities of binary mixtures containing dimethyl sulfoxide (DMSO) + seven normal alkanols, namely methanol, ethanol, propan-1-ol, butan-1-ol, hexan-1-ol, octan-1-ol, and decan-1-ol, have been determined at 303.15 K and atmospheric pressure. With the exception of the DMSO–methanol system, which shows negative values, all mixtures show positive values of excess molar enthalpies over the whole range of mole fraction, increasing as the number of carbon atoms increases. Heat capacities of pure components have been determined in the range $288.15 < T\,(\mathrm{K}) < 325.15$. Molar heat capacities of the mixtures are always positive and decrease as the number of carbon atoms decreases. The results were fitted to the Redlich–Kister polynomial equation. Molecular interactions in the mixtures are interpreted on the basis of the results obtained.

Keywords: Excess enthalpy; Heat capacity; DMSO; Alkanols; Redlich–Kister

1. Introduction

This paper forms part of a series of investigations on the thermo-physical properties of binary mixtures containing dimethyl sulfoxide (DMSO). Excess thermodynamic and bulk properties for binary mixtures of DMSO + glycols and poly (glycols) [1], +esters of carbonic acid [2], +linear and cyclic ethers [3], were reported in our previous works. Excess functions of these binary mixtures are of considerable importance for understanding the nature of molecular interactions. To investigate the size effect of nonpolar groups in *n*-alkanols on the thermo-physical properties of mixtures, excess molar enthalpies, H_m^E, and molar heat capacities, C_p, of mixtures containing DMSO and seven normal alkanols, namely methanol, ethanol, propan-1-ol, butan-1-ol, hexan-1-ol, octan-1-ol, and decan-1-ol, were determined over the whole range of mole fraction at 303.15 K and atmospheric pressure. DMSO is a versatile, nonaqueous, dipolar, aprotic solvent with relative dielectric permittivity $\varepsilon = 46.45$, and dipole moment $\mu = 4.06$ D at 298.15 K [4]. DMSO was chosen because of its wide range of applicability as a solvent in chemical and biological processes, in pharmaceutical applications, in veterinary medicine, and in microbiology [5–7]. Moreover, several properties of this substance have gained attention in relation to cancer [8]. DMSO is also extensively used in kinetic studies [9], and in electrochemistry [10], and serves as a solvent for polymers [11]. Alkanols are the most well known solvents used to study hydrophobic effects. Thermo-physical properties of DMSO + alkanols are of interest because of the possible interactions between S=O groups, and OH groups. Though many works on physical and bulk properties of binary mixtures containing DMSO + alkanols are available in the literature, only a few papers on thermophysical data are known [12–14].

2. Experimental

Sources and purities of chemicals are reported in Table 1. All chemicals were used without further purification and purity values declared by suppliers were confirmed with a Hewlett-Packard G.CX. Model 5890 with an HP (cross-linked 5% ME siloxane) capillary column. Before use, the components were degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy) and dried over molecular sieves (Aldrich, type 3A).

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Table 1
Sources, purities, densities, ρ, and heat capacities, C_p^0, of pure components, heat of vaporization, ΔH_v, and comparison with literature data at 303.15 K

Compound	Source	Purity	ρ (g cm^{-3})		C_p^0 (J mol^{-1} K)		ΔH_v (kJ mol^{-1})
			Experimental	Literature	Experimental	Literature	
DMSO	Fluka	>99.9	1.09045	1.0904 [15]	152.4		
					147.8^a	148.25^a [16]	
Methanol	Aldrich	>99.9	0.78181	0.78182 [17]	82.2		37.43 [4]
					81.0^a	81.26^a [18]	
Ethanol	Merck	99.9	0.78079	0.78076 [19]	115.7		42.3 [4]
					113.5^a	112.36^a [20]	
Propan-1-ol	Aldrich	99.9	0.79548	0.7955 [21]	148.3		47.3 [4]
					144.9^a	144.3^a [22]	
Butan-1-ol	Aldrich	≥99.4	0.80198	0.80203 [23]	178.9	179.2 [24]	52.3 [4]
Hexan-1-ol	Aldrich	≥99	0.81139	0.8115 [25]	246.0	245.02 [26]	61.9 [4]
Octan-1-ol	Fluka	>99.5	0.81824	0.81812 [27]	309.2		71.0 [4]
					304.4^a	304^a [28]	
Decan-1-ol	Aldrich	≥99	0.82295	0.82296 [29]	379.3	373 [29] 383.3 [26]	61.5 [30]

[a] At 298.15 K.

Experimental values of densities, ρ, and heat capacities, C_p^0, of the pure components were compared with literature data [15–30], as shown in Table 1. Density measurements were determined with a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602). The procedure was described elsewhere [31]. The apparatus was calibrated at atmospheric pressure with double-distilled water and dry air, whose densities were taken from literature [32,33].

Density measurements were made at a constant temperature with an external ultrathermostat bath circulator (Heto, type 01 DTB 623, Birkeròd, Denmark, precision ±0.005 K), and temperatures measured by a digital thermometer (Anton Paar, type CTK 100).

The accuracy of the density data are of the order $\pm 1.10^{-5}$ g cm^{-3}.

An isothermal flow calorimeter (LKB, model 2107, Producer AB, Bromma, Sweden) was used to measure the excess molar enthalpy. The apparatus consists of a flow-mixing cell, a reference cell, a thermostatic water bath (±0.01 K), a data acquisition unit, and two liquid burettes (ABU Radiometer, Copenhagen, Denmark). The component mass fractions in the mixed stream were obtained from densities and volumetric flow rates of components 1 (DMSO) and 2 (alkanols). Total flow rates are usually about 0.4 cm^3 min^{-1}, except in dilute regions of DMSO or alkanols where the total flow rates may increase up to 0.8 cm^3 min^{-1}. The uncertainties of mole fraction of each run were estimated to be less than ±0.001. Details and operating procedure of the apparatus have been reported elsewhere [34,35]. The uncertainties of the reported H_m^E values in this study were verified by measurements on three standard systems, cyclohexane + hexane, benzene + cyclohexane, and methanol + water at 298.15 K. Agreement with literature data [36] is better than 0.5% at the maximum of the thermal effect.

Experimental data of excess molar enthalpies, H_m^E, are shown in Supplementary Table 1 and represented in Fig. 1. Fig. 2 reports the values of equimolar H_m^E ($x_1 = 0.5$) as a function of number

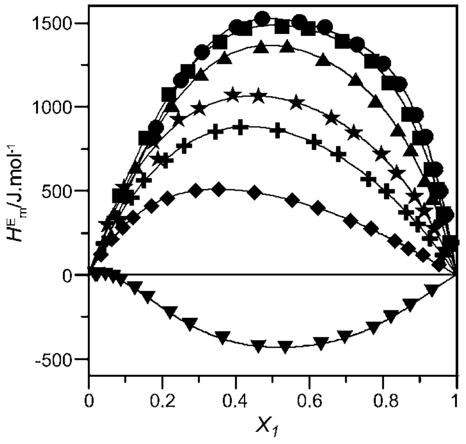

Fig. 1. Excess molar enthalpies, H_m^E, of binary mixtures containing DMSO (1) + alkanols (2) at 303.15 K. ▼, ♦, ✚, ★, ▲, ■, and ● refer to mixtures containing methanol, ethanol, propan-1-ol, butan-1-ol, hexan-1-ol, octan-1-ol, and decan-1-ol, respectively. Full line, Eq. (2).

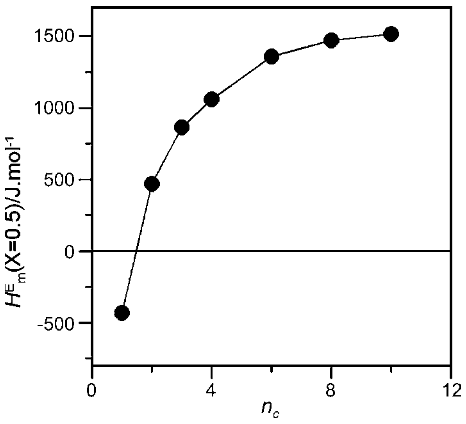

Fig. 2. Values of equimolar H_m^E ($x_1 = 0.5$) as a function of number of carbon atoms n_c in the alkanol molecules.

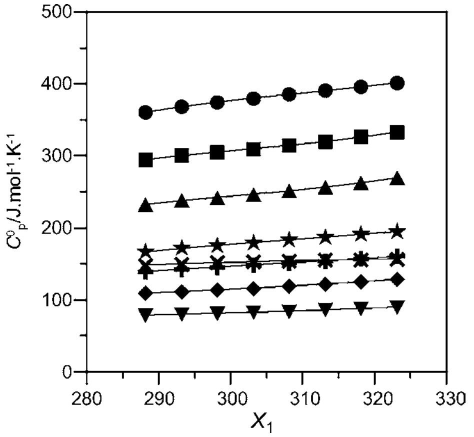

Fig. 3. Liquid heat capacities, C^0_p, of pure components at 303.15 K. ▼, ◆, ✚, ✖, ★, ▲, ■, and ●, refer to methanol, ethanol, propan-1-ol, DMSO, butan-1-ol, hexan-1-ol, octan-1-ol, and decan-1-ol, respectively. Full line, Eq. (1).

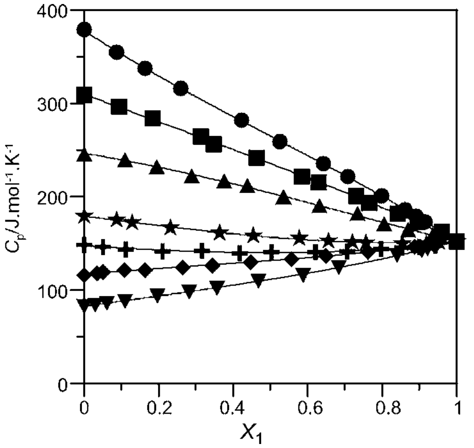

Fig. 4. Molar heat capacities, C_p, of binary mixtures containing DMSO (1) + alkanols (2) at 303.15 K. ▼, ◆, ✚, ★, ▲, ■, and ● refer to mixtures containing methanol, ethanol, propan-1-ol, butan-1-ol, hexan-1-ol, octan-1-ol, and decan-1-ol, respectively. Full line, Eq. (1).

n_C of carbon atoms in the alkanol molecules. The uncertainty of H^E_m values is of the order 1%.

The heat capacity measurements were performed with a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a model PII intracooler. The instrument was calibrated with high-purity standards (indium and cyclohexane) at 5 K min^{-1}. The temperature was known to within ±0.1 K. The samples, approximately 10 mg, determined to ±0.01 mg, were encapsulated in hermetic pans. The heat capacity of the samples was obtained by means of three consecutive DSC runs at scanning rate of 5 K min^{-1}: the sample run, the blank run and the standard sample (sapphire) run [37]. Care was taken to ensure that similar initial and final isotherm levels were reached for all three scans. The heat capacity data were obtained by means of the commercial software supplied by Perkin-Elmer. The estimated uncertainty for repeated data is less than 0.1%.

The experimental heat capacities, C^0_p, of pure components (from 288.15 to 323.15 K) versus the temperature T (K), at normal pressure, are listed in Supplementary Table 2 and represented in Fig. 3. Supplementary Table 3 reports the experimental values of the molar heat capacities, C_p, of mixtures versus the mole fraction, x_1, of DMSO which are represented in Fig. 4. The expression used to fit both C^0_p and C_p values is

$$C_p = c_0 + c_1(T(\mathrm{K})) + c_2(T(\mathrm{K}))^2 \tag{1}$$

Values of the parameters c_k are listed in Tables 2 and 3 together with the standard deviations σ (C_p).

Experimental excess molar enthalpies, H^E_m were fitted by the method of least squares, with all points weighted equally, to the smoothing Redlich–Kister polynomial

$$H^\mathrm{E}_\mathrm{m} = x_1x_2\sum_{k\geq 0}a_k(x_1 - x_2)^k \tag{2}$$

The adjustable parameters, a_k, were determined by a least-squares method, fitting the experimental values to Eq. (2) and the results are given in Table 4. The standard deviations, σ $(H^\mathrm{E}_\mathrm{m})$, reported in Table 4 were defined as

$$\sigma(H^\mathrm{E}_\mathrm{m}) = \left|\frac{\phi_\mathrm{min}}{N - n}\right|^{0.5} \tag{3}$$

with N and n the number of experimental points and parameters, respectively, whereas ϕ_min is the minimum value of the objective function ϕ defined as

$$\phi = \sum_{k=1}^{N}\eta_k^2 \tag{4}$$

Table 2
Adjustable parameters of Eq. (1) and standard deviation, σ (C^0_p) of pure components

Component	c_0	c_1	c_2	σ (C_p) (J mol^{-1} K^{-1})
DMSO	−232.62	2.2738	−0.0033	0.4
Methanol	255.49	−1.4523	0.0029	0.2
Ethanol	354.37	−2.1076	0.0044	0.2
Propan-1-ol	−15.197	0.4807	0.0002	0.2
Butan-1-ol	−178.66	1.5626	−0.0013	0.5
Hexan-1.ol	509.74	−2.7466	0.0062	0.6
Octan-1-ol	543.02	−2.5830	0.0060	0.6
Decan-1-ol	−463.87	4.3921	−0.0053	0.7

Table 3
Adjustable parameters of Eq. (1) and standard deviation, σ (C_p) of binary mixtures containing DMSO + normal alkanols at 303.15 K

Mixture	c_0	c_1	c_2	σ (C_p) (J mol^{-1} K^{-1})
DMSO + methanol	82.915	45.171	23.464	0.7
DMSO + ethanol	117.42	22.510	11.681	0.8
DMSO + propan-1-ol	148.07	−34.795	37.506	0.9
DMSO + butan-1-ol	179.88	−64.852	36.245	0.7
DMSO + hexan-1-ol	247.46	−78.466	−17.729	1.3
DMSO + octan-1-ol	309.50	−140.25	−14.564	1.4
DMSO + decan-1-ol	375.65	−218.54	−2.7862	1.9

Table 4
Adjustable parameters, a_k, Eq. (2), and standard deviations σ (H_m^E), Eq. (3), of DMSO + normal alkanols at 303.15 K

Function	a_0	a_1	a_2	a_3	a_4	σ (H_m^E)
DMSO (1) + methanol (2), H_m^E (J mol^{-1})	−1731.1	−168.53	213.10	−797.58	1277.2	2.6
DMSO (1) + ethanol (2), H_m^E (J mol^{-1})	1876.4	−923.83	718.14	−438.99		3.1
DMSO (1) + propan-1-ol (2), H_m^E (J mol^{-1})	3469.3	−830.53	573.35			5.8
DMSO (1) + butan-1-ol (2), H_m^E (J mol^{-1})	4215.7	−755.86	1661.0			7.2
DMSO (1) + hexan-1-ol (2), H_m^E (J mol^{-1})	5464.6	−159.35	1397.4	1489.5		5.2
DMSO (1) + octan-1-ol (2), H_m^E (J mol^{-1})	5945.4	85.778	2531.0	2656.2		6.9
DMSO (1) + decan-1-ol (2), H_m^E (J mol^{-1})	6099.7	−150.07	2300.5	4961.2		8.3

where $\eta_k = H_{m,calcd}^E - H_m^E$. H_m^E is the experimental value and $H_{m,calcd}^E$ is evaluated through Eq. (2).

3. Results and conclusions

Our H_m^E data are comparable with that of Kimura et al. [12], whereas Chao et al. [38] report measurements disagreeing strongly. Kimura et al. have analyzed and discussed that discrepancy [12].

Figs. 1 and 4 report the calorimetric data of this paper, H_m^E and C_p, showing a regular trend with increasing number n_c of carbon atoms.

Qualitative interpretation of the curves is allowed by the approximate expression $H_m^E \propto E_{11} + E_{22} - 2E_{12}$, where E_{ij} is the interaction energy between molecules i and j. Self-association of alkanols and interaction between OH group of alkanols and S=O group of DMSO must be accounted for. The trend of H_m^E may be explained by considering that: (1) E_{11} increases with n_c (see Table 1 reporting enthalpies of vaporization of alkanols, proportional to E_{11}), (2) the increasing chain length in alkanols leads to a reduction in the interaction E_{12} between the OH of alkanols and the S=O of DMSO.

The C_p°s of pure compounds in Fig. 3 show a regular increase with increasing temperature, with a slope that slightly increases with the number n_c of carbon atoms. The molar heat capacities, C_p, of the binary mixtures, see Fig. 4, show a composition dependence going gradually from a negative to a positive slope, with C_p nearly independent of molar fraction for $n_c = 3$ and 4.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.10.025.

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