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Excess molar enthalpies of dimethylsulfoxide with chloroethanes and chloroethenes at 298.15 K

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Abstract

Excess molar enthalpies (H_M^E) at 298.15 K and ambient pressure have been measured as a function of composition for the binary liquid mixtures of dimethylsulfoxide (DMSO) with chloroethanes and chloroethenes. The chloroethanes include 1,2-dichloroethane, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane and the chloroethenes are trichloroethene and tetrachloroethene. The H_M^E values for the above mixtures have been measured by a Paar 1451 solution calorimeter and are negative over the whole range of composition in all the binary mixtures except in the binary system of DMSO with tetrachloroethene, whereas the H_M^E is positive over the entire range of composition. The experimental results have been correlated using the Redlich–Kister (R–K) polynomials and the results are interpreted on the basis of possible hydrogen bonding between unlike molecules and changes in molecular association equilibria as well as structural effects for these systems. The excess molar enthalpy data have also been correlated with the Peng–Robinson (PR) as well as the Patel–Teja (PT) equations of state (EOS) and also the activity coefficient models of the Wilson and the NRTL.

Keywords: Excess molar enthalpies; Binary mixture; Dimethylsulfoxide; Chloroethanes and chloroethenes; Molecular interactions; Theoretical models

1. Introduction

Experimental data of excess thermodynamic properties of liquids and liquid mixtures are fascinating and of great fundamental, practical importance, theoretical and industrial points of view. Moreover, these properties allow one to draw information on the structure and interactions of mixed solvents. The chemical industries have recognized the importance of the thermodynamic properties in design calculations involving chemical separations, heat transfer, mass transfer and fluid flow. The thermodynamic properties of dimethylsulfoxide (DMSO) have been the subject of considerable interest because of its versatility as a solvent in chemical and biological processes and a plasticizer. DMSO is a dipolar, aprotic, hygroscopic solvent for which a large number of pharmacologic properties have been claimed. It also exerts a solvent effect sufficient to accelerate a reaction brought about by another reagent. It is less toxic and an effective paint stripper, being much safer than many of the other polar solvents. Since, DMSO as a solvent of its high boiling point, thus its solutions are not typically evaporated but instead diluted to isolate the reaction product. It is a versatile organic liquid having a special solvent power to promote a chemical reaction when used as a reaction medium. It is also used as a solvent for polymerization reactions displacement reactions because of its high dielectric constant value ($\varepsilon = 46.45$) [1]. Moreover, it is a highly polar self-associated ($\mu = 4.06$ D) [1] liquid and has ability to participate in hydrogen bonding. In liquid mixtures, the enhancement of its donor ability may result from the breaking of DMSO structure by the addition of second liquid component [2].

Chlorinated compounds are extensively used in industrial, agricultural and commercial processes as solvents, lubricants, intermediates in chemical industry, pesticides, pharmaceuticals and medical equipment. The physical and chemical properties of chloroethenes differ strikingly from those of saturated aliphatic chlorine compounds. In recent years, the thermodynamic

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properties of highly polar compounds with chloroethanes and chloroethenes have received increasing attention because they serve as model compounds in biochemical considerations [3–6]. DMSO, chloroethanes and chloroethenes are important liquids, which find a variety of applications such as solvents for lacquers, oils and resins [5]. These liquids were chosen in the present investigation on the basis of their industrial importance. Thermodynamic properties of these solvents are of interest because of the effect of chlorine with S=O group present in the DMSO on the molecular interactions.

The excess molar enthalpy (H_M^E) of binary mixtures containing DMSO + cycloethers [7], +1,1,2,2-tetrachloroethane at 308.15 K [8], +hexamethylphosphoric trimide [9], +water [10], +dialkylethers [11], +halogenized aromatic compounds [12,13], +dihalogenized benzenes [14], +*N*,*N*-dimethylethanolamine [15], +alkylbenzenes [16], +1-alkynes [17], +alkane-1-amines [18], +aliphatic alcohols [19], +aliphatic alcohols or aliphatic nitriles [20], +normal alcohols [21] have been appeared in the literature. However, no effort appears to have been made to collect H_M^E for the mixtures of DMSO with chloroethanes and chloroethenes and there is no evidence for specific interactions between DMSO with chloroethanes and chloroethenes. Molar excess enthalpies of these mixtures are also of interest from thermodynamic and structural points of view. In order to extend our research programs to explore the interactions between the highly polar groups with other solvents [3,22–29], and to characterize the type and magnitude of molecular interactions between the polar group solvents, we report here the H_M^E at 298.15 K and atmospheric pressure of binary mixtures containing DMSO with 1,2-dichloroethane, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane and chloroethenes include trichloroethene and tetrachloroethene. Moreover, the H_M^E data were correlated with the Peng–Robinson (PR) [30] and the Patel–Teja (PT) [31] equations of state and also the activity coefficient models of the Wilson [32] and the NRTL [33] for the binary systems.

2. Experimental

2.1. Materials

The commercially available pure solvents of highest purity were used in the present investigation. DMSO, chloroethanes and chloroethenes were purified by the standard methods described by Riddick et al. [1]. The purity of the samples was checked by measuring densities and boiling points. The densities were measured using a standard bicapillary pycnometer, giving an accuracy of two parts in 10^5. Boiling points were measured by Swietoslawski type ebulliometer [34] with an accuracy of ±0.2 K. The purities of the samples were further confirmed by GLC single sharp peaks. Good agreement between the measured densities as well as boiling points and literature [1,3,35] values is shown in Table 1.

2.2. Apparatus

The H_M^E values of liquid mixtures were measured using a Paar 1451 solution calorimeter. The measurements were performed in an isolated house at 298.15 K and atmospheric pressure. The detailed procedure and apparatus used in this work have been depicted in our previous papers [23,36]. In the measurement of excess enthalpies, known mass of 100 ml of one component A as solvent is taken into the Dewar vessel and 20 ml of other component B as solute is weighed in a sealed glass rotating cell. Both the components are kept in thermal contact with each other in the Dewar mixing chamber at 298.15 K. After attaining the thermal equilibrium, component B in the rotating cell is mixed with component A in the Dewar vessel by pushing the glass rod. The temperature change accompanying the mixing process is sensed by the thermistor and recorded on the strip chart recorder. These experiments were continued until the concentrations reach 50–60% and this procedure was repeated by taking solvent as solute and solute as solvent. The reliability of the apparatus and the method was established by measuring H_M^E values of standard systems, i.e., benzene with carbontetrachloride and chlorobenzene with toluene throughout the concentration range at 298.15 K. Results were in good agreement with the reported data in the literature [37]. The uncertainty of the measured H_M^E values is ±1%.

3. Results and discussion

The measured H_M^E values of DMSO with chloroethanes and chloroethenes at 298.15 K are graphically represented in Fig. 1 (and also reported in Supplementary data as a table) as a function of mole fraction of chloroethanes or chloroethenes. The experimental H_M^E results of each binary system were fitted

Table 1
Densities (ρ) at 303.15 K and boiling point temperatures (T_b) at 101.3 kPa

Component	ρ (g cm^{-3})		T_b (K)	
	Experiment	Literature	Experiment	Literature[a]
DMSO	1.092 40	1.091 42[b]	462.19	462.15
1,2-Dichloroethane	1.238 41	1.238 43[c]	356.95	356.63
1,1,1-Trichloroethane	1.320 97	1.320 94[c]	347.35	347.23
1,1,2,2-Tetrachloroethane	1.578 59	1.578 57[c]	418.35	418.13
Trichloroethene	1.451 42	1.451 39[c]	360.25	360.34
Tetrachloroethene	1.606 39	1.606 41[c]	394.15	394.22

[a] Ref. [1].
[b] Ref. [35].
[c] Ref. [24].

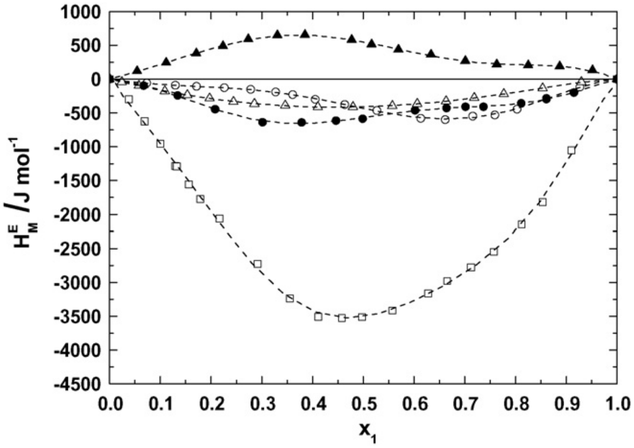

Fig. 1. Excess molar enthalpies (H_M^E) of DMSO with 1,2-dichloroethane (○), 1,1,1-trichloroethane (△), 1,1,2,2-tetrachloroethane (□), trichloroethene (●), or tetrachloroethene (▲) at 298.15 K and at atmospheric pressure against mole fraction (x_1). Dashed lines (– – –) correlated by the Redilich–Kister equation.

with the smoothing functions by the Redilich–Kister (R–K) type equation using the polynomial form:

$$H_M^E\,(\mathrm{J\,mol^{-1}}) = x_1(1-x_1)\sum_i h_i(2x_1-1)^i \tag{1}$$

where h_i are the coefficients for the binary mixtures and are collected in Table 2 along with the percentage standard deviation. The values of the percentage standard deviation are computed from the relation:

$$\%\sigma(H_M^E)=\left[\frac{\sum_{i=1}^{n}[100\times(H_{\mathrm{M\,calc},i}^E-H_{\mathrm{M\,expt},i}^E)/H_{\mathrm{M\,expt},i}^E)]^2}{n-p}\right]^{0.5} \tag{2}$$

where n and p are the numbers of data points and parameters, respectively. As can be seen in Fig. 1, the R–K equation correlates satisfactorily for these binary mixtures.

The H_M^E data have been correlated using the PR [30] and the PT [31] equations of state and also the activity coefficient models of the Wilson [32] and the NRTL [33] for all the binary systems. The properties of pure compounds are collected in Table 3. The calculated H_M^E data from the various models are also included in Supplementary data as a table. The correlated results of the equations of state (the PR and the PT) and the activity coefficient models (the Wilson and the NRTL) are reported in Tables 4 and 5, respectively. The value of randomness, α, in the NRTL model was specified to be 0.3 in the calculation for each binary system.

From Fig. 1, it can be seen that the H_M^E values are negative (−ve) (exothermic) in the mixtures of DMSO with chloroethanes or trichloroethene at 298.15 K over the whole range of composition. On the other hand, the positive (+ve) (endothermic) H_M^E values have been observed in the mixtures of DMSO with tetracholoroethene under the same experimental conditions. The exothermic nature of these results is a reflection of the dominance of the strong association between DMSO with chloroethanes. The strongest association was between DMSO and 1,1,2,2-tetrachloroethane and may be due to stabilization of DMSO. In other words, the H_M^E values at 308.15 K of DMSO with 1,1,2,2-tetrachloroethane (at equimolar composition $H_M^E = -3285\,\mathrm{J\,mol^{-1}}$), which is in fair agreement with the value reported in the present study (at equimolar composition $H_M^E = -3514\,\mathrm{J\,mol^{-1}}$ at 298.15 K). Usually, the association effect decreases as substitution on the ethane molecule decreases. Our results are consistent with this phenomenon, i.e., the least exothermic effect has been occurred in the system of DMSO with 1,2-dichloroethane (Fig. 1). The maximum positive or negative H_M^E value is observed around 0.4–0.6 mole fraction of DMSO.

Excess molar enthalpy data may be interpreted by considering the following factors: (a) loss of dipolar association due to the addition of one component to the other, and difference in

Table 2
Estimated parameters of Eq. (1) and percentage of standard deviation % $\sigma(H_M^E)$ for the mixtures of DMSO with chloroethanes or chloroethenes at 298.15 K

Component 1	h_0 (J mol^{-1})	h_1 (J mol^{-1})	h_2 (J mol^{-1})	h_3 (J mol^{-1})	%$\sigma(H_M^E)$
1,2-Dichloroethane	1729	−3118	−657	4329	2.5
1,1,1-Trichloroethane	−1633	488	89	−251	1.4
1,1,2,2-Tetrachloroethane	−14906	2759	16,244	−20002	2.1
Trichloroethene	−2291	2187	−1,285	6779	2.5
Tetrachloroethene	2222	−2595	−1,164	3629	2.7

Table 3
Properties of pure components

Compound	MW[a] (g mol^{-1})	T_c[a] (K)	P_c[a] (MPa)	ω[a]	V_L[b] (cm^3 mol^{-1})
DMSO	78.13	729.00	5.65	0.2805	71.33
1,2-dichloroethane	98.96	561.60[c]	5.38[c]	0.2865	79.91
1,1,1-trichloroethane	133.40	548.40[c]	4.30	0.2182	100.31
1,1,2,2-tetrachloroethane	167.85	644.50[c]	4.09	0.2466	105.79
Trichloroethene	131.39	571.00	4.85	0.2166	89.76
Tetrachloroethene	165.83	620.00	4.49	0.2137	103.61

[a] Aspen Plus databank.
[b] Calculation results from densities and molecular weight.
[c] NIST.

Table 4
Correlated results from the equations of state

Component 1	PR		PT	
	$k_{a_{ij}}$	AAD H_M^E (%)	$k_{a_{ij}}$	AAD H_M^E (%)
1,2-Dichloroethane	−0.0099	35.1	−0.0098	35.1
1,1,1-Trichloroethane	−0.0374	22.6	−0.0372	22.6
1,1,2,2-Tetrachloroethane	−0.1552	16.8	−0.1542	16.9
Trichloroethene	−0.0337	14.4	−0.0335	14.4
Tetrachloroethene	0.0078	25.8	0.0078	25.8
Grand AAD H^E (%)		22.9		22.9

size between unlike molecules and (b) dipole-induced dipole and dipole–dipole interactions and electron donor–acceptor complex formation. Formation of electron donor–acceptor complexes between the components of these mixtures is possible due to the fact that DMSO acts as an electron donor and the chlorinated ethanes and ethenes act as an electron acceptor. The former factor results in endothermic event of mixing, i.e., positive values for H_M^E, where as the latter effect, would contribute to exothermic process of mixing, i.e., negative values for H_M^E. The actual sign and magnitude of H_M^E depend on the dominant factor. The positive H_M^E values in the mixture of DMSO with tetrachloroethene were suggested that the property of this mixture is determined by the loss of dipolar association by the addition of one component to the other and the difference in size and shape of the component molecules. The experimental negative excess enthalpies for the mixtures of DMSO with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane and trichloroethylene are determined by the dipole-induced dipole interactions and the electron donor–acceptor complex formation.

The algebraic values of H_M^E fall in the order:

$$\begin{aligned} &\text{tetrachloroethene} > 1,2\text{-dichloroethane} \\ &> 1,1,1\text{-trichloroethane} > \text{trichloroethene} \\ &> 1,1,2,2\text{-tetrachloroethane} \end{aligned}$$

It is noteworthy to compare H_M^E of DMSO with chloroethanes and chloroethenes at 298.15 K with those of the highly polar solvent of *N*-methyl-2-pyrrolidinone (NMP). Analogously, a similar trend has been observed in our earlier work [4] for NMP with chloroethanes and chloroethenes at 298.15 K.

4. Data correlation

The Peng–Robinson [30] and the Patel–Teja [31] equations of state were also applied to correlate the H_M^E data. The van der Waals one-fluid mixing rules incorporating with a single binary interaction parameter, $k_{a_{ij}}$, were adopted in the enthalpy calculation. The combining rule of a_{ij} was defined as

$$a_{ij} = (1 - k_{a_{ij}})(a_i a_j)^{0.5} \tag{3}$$

The optimal value of $k_{a_{ij}}$ was determined by minimization of the following objective function:

$$\text{AAD } H_M^E(\%) = \frac{100}{n}\sum_{i=1}^{n}\frac{|H_{M\,\text{calc},i}^E - H_{M\,\text{expt},i}^E|}{H_{M\,\text{expt},i}^E} \tag{4}$$

Where AAD is the average absolute deviation and n is the number of data points. Table 4 lists the correlated results from these two equations of state. The calculated results from both two equations of state are almost the same, a grand AAD of 22.9%. The Wilson and the NRTL models were also used to correlate H_M^E data. The optimal values of the model parameters and correlated results are listed in Table 5. The randomness, α, in the NRTL model was fixed as 0.3. In comparing with the results from the equations of state, those from the Wilson and the NRTL models are obviously better with grand AADs of 16.0% and 15.5%, respectively. However, it should also be noted that two adjustable parameters were included in the activity coefficient models, whereas only one parameter was employed in the equations of state.

Table 5
Correlated results from the activity coefficient models

Component 1	$(\lambda_{12}–\lambda_{11})/R$ (J mol^{-1})	Wilson			NRTL		
		$(\lambda_{21}–\lambda_{22})/R$ (J mol^{-1})	AAD H_M^E (%)	$(g_{12}–g_{22})$/R (K)	$(g_{12}–g_{11})/R$ (K)	α	AAD H_M^E (%)
1,2-Dichloroethane	−33.09	454.05	22.7	−192.45	229.61	0.3	29.5
1,1,1-Trichloroethane	−296.60	593.09	7.8	4969.93	−108.59	0.3	10.3
1,1,2,2-Tetrachloroethane	−556.17	−274.24	15.2	−534.40	89.63	0.3	7.2
Trichloroethene	−172.84	−50.39	14.2	−65.22	−172.60	0.3	14.2
Tetrachloroethene	252.94	106.95	20.1	−6.98	396.80	0.3	18.0
Grand AAD H^E (%)			16.0				15.5

5. Conclusions

Excess molar enthalpies have been measured experimentally for binary mixtures of DMSO with chloroethanes and chloroethenes at 298.15 K over the entire range of compositions. The excess molar enthalpy data have also been correlated with the Peng–Robinson (PR) as well as the Patel–Teja (PT) equations of state (EOS) and also the activity coefficient models of the Wilson and the NRTL. The H_M^E values for the mixtures of DMSO with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane and trichloroethene are negative over the whole range of composition whereas the H_M^Evalues are positive over the entire range of composition in the binary system of DMSO with tetrachloroethene.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.08.008.

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