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## Study of Solvent-Solvent Interactions in Acetonitrile-Dimethylsulphoxide Mixtures

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ABSTRACT: The refractive indices, dielectric constants, densities, vapour pressures and viscosities of acetonitrile (MeCN)-dimethylsulphoxide (DMSO) mixtures were determined. The data point to deviations from ideality confirming the existence of solvent-solvent interactions. These interactions appear to reach a maximum in the 1 : 1 mole ratio and are confirmed from Infra-red and Raman spectra of solvent mixtures.

Over the last ten years charge-transfer complexes of the type  $\text{SO}_2\text{-X}^-$ ,  $\text{SOCl}_2\text{-X}^-$ ,  $\text{SOBr}_2\text{-X}^-$ ,  $\text{SO}_2\text{Cl}_2\text{-X}^-$ ,  $\text{SeO}_2\text{-X}^-$  and  $\text{SeOCl}_2\text{-X}^-$  ( $\text{X}^- = \text{Cl}, \text{Br}, \text{I}$  and  $\text{SCN}$ ) were identified and their thermodynamic parameters determined in MeCN, DMSO and their mixtures over the temperatures 10-35°C. The stability constants in the MeCN-DMSO mixed solvents pointed to the existence of solute-solvent and solvent-solvent interactions (Salama and Wasif 1971, 1973, 1975a and b, 1978, 1980). Solute solvent interactions were shown to exist (Salama and Wasif 1971, 1973, 1975a) and in fact account for the change in stability constants of the above complexes in MeCN and DMSO by solvation of halide ligands and adduct formation between solvent molecules and sulphur acceptor molecules.

The present work aims to confirm the existence of solvent-solvent interactions predicted earlier (Salama and Wasif 1978, 1980).

### Experimental

#### *Materials*

Dimethylsulphoxide, acetonitrile and cyclohexane were Merck products of spectroscopic quality. The refractive indices, dielectric constants and densities were measured and agreed satisfactorily with literature values (Waddington 1965).

### Techniques

The present work required several techniques to be used which are briefly outlined as follows:

#### a) *Refractive Indices, Dielectric Constants, Densities and Their Excess Functions*

The refractive indices of the pure solvents and their mixtures were measured with a Carl Zeiss Jena immersion refractometer at 298.15 K. The dielectric constants were measured with a dielectrometer which operates at 2 MHz. The cell was a stainless steel cylinder of the MFL 3/S type with a dielectric constant measuring range of 21 to 90 at 298.15 K. The density measurements were performed with an Anton Paar model DMA 10 vibrating tube densitometer. It was calibrated with dry air, distilled water and absolute alcohol and use of equation (1)

$$\rho = K(t_1^2 - t_2^2) \quad (1)$$

where  $\rho$  is the density;  $t_1$  and  $t_2$  are the vibrating frequencies.

The excess functions for refractive index  $n^E$ , dielectric constant  $\epsilon^E$  and volume  $V^E$  were fitted to the Redlich-Kister equation (1948) as:

$$n^E = x_1x_2(A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 + \dots) \quad (2)$$

and a computer program was used to find the coefficients  $A_0 \dots$  and the standard deviation ( $\sigma$ ) for each function. The values of  $A$  and  $\sigma$  will be given in each table.

#### b) *Vapour Pressure and Viscosity*

Vapour pressures of pure and mixed solvents were measured by the isoteniscope method suggested by Smith and Menzies (1910), while the viscosity was measured by a calibrated Ostwald's viscometer. All measurements were carried out over a certain range of temperatures selected for each solvent mixture. The thermodynamic values ( $\Delta H_{\text{vap}}^\circ$  and  $\Delta H_{\text{vis}}^\circ$ ) were calculated using computer programme, Table 5.

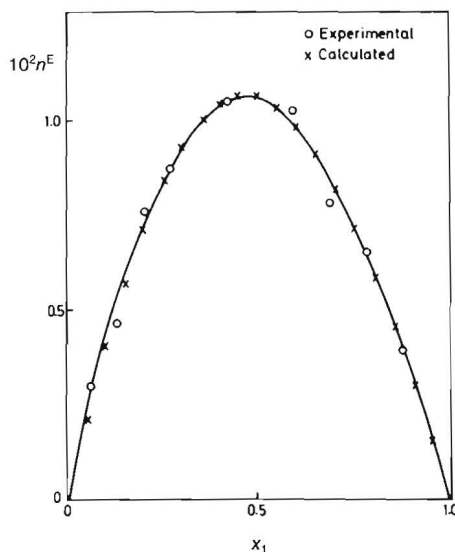
#### c) *Infra-red Spectroscopy*

Cyclohexane solutions of MeCN, DMSO and their mixtures of mole ratios 1 : 1, 1 : 2, 1 : 4 and 1 : 6 were prepared and two sets were studied. In one set, (MeCN) concentration was kept constant while (DMSO) was varied and the spectra measured in the range 1000-1100  $\text{cm}^{-1}$ . In the second set, (DMSO) was kept constant and (MeCN) varied and the measurements were done in the range 2200-2300  $\text{cm}^{-1}$ . The spectra were measured against cyclohexane as reference. A Perkin-Elmer grating spectrophotometer model 457 was used. The slit width was normal and cells were equipped with KBr windows path length of 0.2 mm.

**Table 1.** Excess refractive indices  $n^E$  of MeCN-DMSO mixtures at 298.15 K.

$x_1$	0.0000	0.1319	0.1982	0.2676	0.4258	0.6009
$n^E$	0.0000	0.0047	0.0076	0.0087	0.0104	0.0102
$x_1$	0.6899	0.7836	0.8697	1.0000		
$n^E$	0.0078	0.0065	0.0039	0.0000		

$A_0 = +0.0425$   $A_1 = -0.0069$   $A_2 = -0.0057$   $\sigma = 0.0003 \text{ cm}^3/\text{mol}$ .  
 $x_1$  represents the mole fraction of DMSO.

**Fig. 1.** Plot of  $n^E$  against  $x_1$  at 298.15 K

#### d) Raman Spectroscopy

They were recorded on a Coderg PHO Raman spectrophotometer using exciting radiation at 647.1 from a coherent radiation krypton laser. The following mole ratios were used:

solution	1	2	3	4	5
(MeCN)/(DMSO)	0.3	0.5	1	2	3

### Results and Discussion

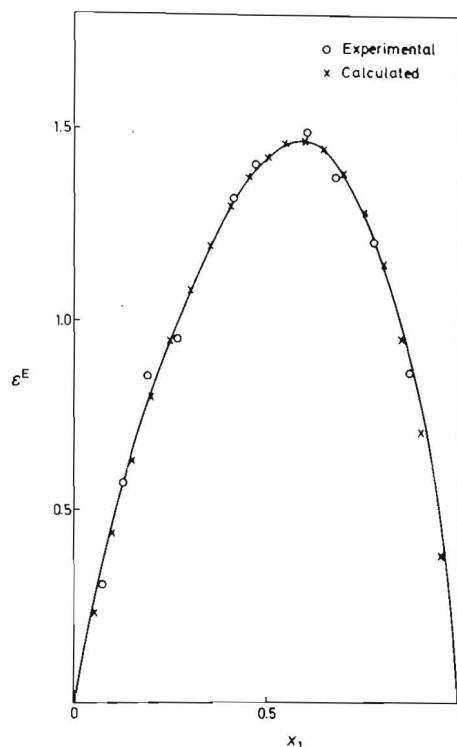
#### a) Excess Functions $n^E$ , $\epsilon^E$ and $V^E$ as Evidence of Solvent-Solvent Interactions

Data of the excess functions  $n^E$ ,  $\epsilon^E$  and  $V^E$  summarised in Tables 1-4 and

**Table 2.** Excess dielectric constants  $\epsilon^E$  of DMSO-MeCN mixtures at 298.15 K.

$x_1$	0.0000	0.0760	0.1319	0.1982	0.2676	0.4258	0.4755
$\epsilon^E$	0.0000	0.2990	0.5710	0.8580	0.9540	1.3180	1.4040
$x_1$	0.6009	0.6899	0.7836	0.8697	1.0000		
$\epsilon^E$	1.4910	1.3680	1.1960	0.8630	0.0000		

$$A_0 = +5.6929 \quad A_1 = +1.7902 \quad A_2 = +1.0179 \quad \sigma = 0.03 \text{ cm}^3/\text{mol}.$$

**Fig. 2.** Plot of  $\epsilon^E$  against  $x_1$  at 298.15 K

graphically represented in Fig. 1-3, confirm that solvent-solvent interaction reaches a maximum at 0.5 mole fraction.

The negative values of  $V^E$  indicate that molecular interaction between MeCN and DMSO exists and is in fact accompanied by volume contraction. This process passes through dissociation of the self-associated molecules in the pure solvents and their association as they are mixed together. The association is favoured by increasing the temperature as shown in Fig. 3.

**Table 3.** Excess volumes  $V^E$  of MeCN-DMSO mixtures at 298.5 K.

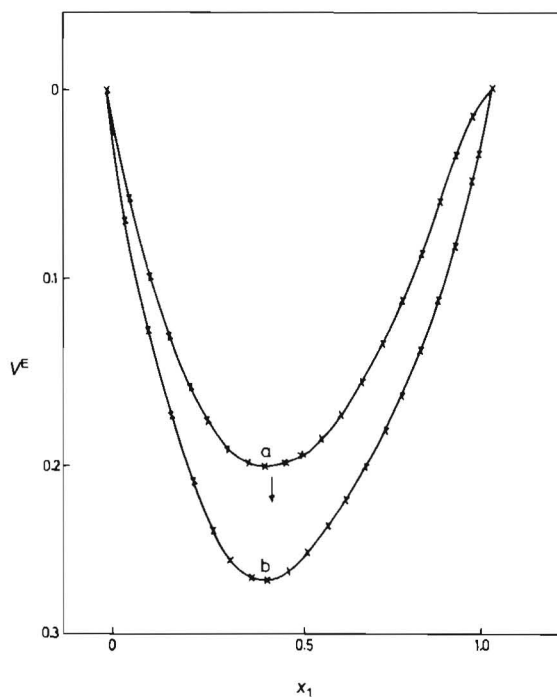
$x_1$	0.0000	0.1006	0.2025	0.3086	0.4057	0.5032
$V^E \text{ cm}^3 \text{ mol}^{-1}$	0.0000	-0.0974	-0.1546	-0.1908	-0.2028	-0.1892
$x_1$	0.6037	0.7061	0.8083	0.8503	0.8999	0.9455
$V^E \text{ cm}^3 \text{ mol}^{-1}$	-0.1648	-0.1307	-0.0888	-0.0541	-0.0399	-0.0011
$x_1$	1.0000					
$V^E \text{ cm}^3 \text{ mol}^{-1}$	0.0000					

$A_0 = -0.7720 \text{ cm}^3/\text{mol}$   $A_1 = +0.2800 \text{ cm}^3/\text{mol}$   $A_2 = +0.6529 \text{ cm}^3/\text{mol}$   $A_3 = +0.2557 \text{ cm}^3/\text{mol}$   
 $\sigma = 0.006 \text{ cm}^3/\text{mol}$ .

**Table 4.** Excess volumes values  $V^E$  of MeCN-DMSO mixtures at 313.5 K.

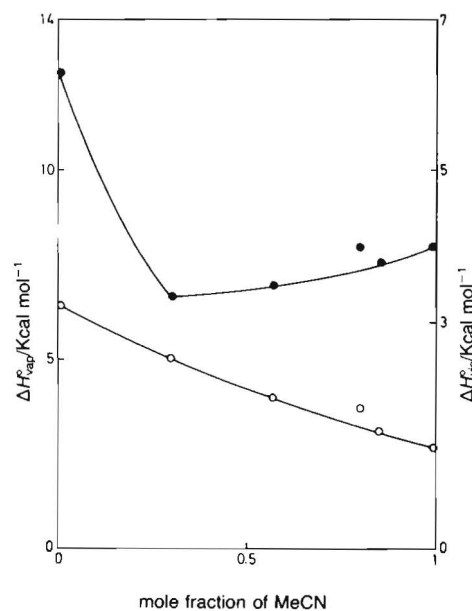
$x_1$	0.0000	0.1006	0.2025	0.3086	0.6037	0.7061
$V^E \text{ cm}^3 \text{ mol}^{-1}$	0.0000	-0.1300	-0.2037	-0.2523	-0.2159	-0.1773
$x_1$	0.8083	0.8503	0.8999	0.9455	1.0000	
$V^E \text{ cm}^3 \text{ mol}^{-1}$	-0.1275	-0.1113	-0.0876	-0.0586	0.0000	

$A_0 = -0.9750 \text{ cm}^3/\text{mol}$   $A_1 = +0.4499 \text{ cm}^3/\text{mol}$   $A_2 = +0.2739 \text{ cm}^3/\text{mol}$   $A_3 = -0.2721 \text{ cm}^3/\text{mol}$   
 $\sigma = 0.004 \text{ cm}^3/\text{mol}$ .

**Fig. 3.** Plot of  $V^E$  against  $x_1$  at  
a: 298.5 K  
b: 313.5 K

**Table 5.** Thermodynamic data of vaporisation and viscosity.

Mole fraction of MeCN in solvent mixture	$\Delta H_{\text{vap}}^{\circ}$ Kcal mol <sup>-1</sup>	$\Delta S_{\text{vap}}^{\circ}$ cal K <sup>-1</sup> mol <sup>-1</sup>	$\Delta H_{\text{vis}}^{\circ}$ Kcal mol <sup>-1</sup>
1.00	7.94	22.94	1.31
0.85	7.59 ± 0.28	20.81 ± 0.92	1.57 ± 0.05
0.80	7.95 ± 0.1	21.84 ± 0.32	1.85
0.57	6.95 ± 0.43	18.13 ± 0.14	1.97 ± 0.04
0.30	6.75 ± 0.25	14.98 ± 0.75	2.53 ± 0.07
0.00	12.64 ± 0.10	22.9	3.19

**Fig. 4.** Plot of  $\Delta H_{\text{vap}}^{\circ}$  (●)  
 $\Delta H_{\text{vis}}^{\circ}$  (○)  
against mole fraction of MeCN

#### b) Enthalpies of Vaporisation and Viscosity as Evidence of MeCN-DMSO Interaction

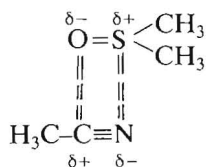
The existence of molecular interaction between acetonitrile and dimethyl-sulphoxide with possible formation of 1 : 1 adducts has been confirmed by the thermodynamic data for vaporisation and viscosity ( $\Delta H_{\text{vap}}^{\circ}$  and  $\Delta H_{\text{vis}}^{\circ}$ ) included in Table 5 and graphically represented in Fig. 4.



### c) *Infra-Red Spectra*

For DMSO in pure cyclohexane the S = O vibration band appears at 1080  $\text{cm}^{-1}$ . On addition of MeCN (at 1 : 1 mole ratio) the band is shifted to 1070  $\text{cm}^{-1}$  and remains unchanged at higher MeCN ratios. For the C  $\equiv$  N vibration band in MeCN the band appears at 2250  $\text{cm}^{-1}$ . At  $x_1 = 0.5$  this band is shifted to 2240  $\text{cm}^{-1}$  with a decrease in its intensity.

The observed band shifts may be taken as evidence of adduct formation possibly of the type:



### d) *Raman Spectra*

For DMSO, the S = O band appears at 1044  $\text{cm}^{-1}$ . On addition of MeCN a peak appears at 1062  $\text{cm}^{-1}$  while that at 1044  $\text{cm}^{-1}$  nearly disappears.

For MeCN the C  $\equiv$  N band appears at 2255  $\text{cm}^{-1}$ . Addition of DMSO does not shift this band but the peak intensity decreases with increase in the mole ratio of DMSO. The observed band changes are considered as supplementary evidence for solvent-solvent interaction which is now believed to exist in polar mixed solvent systems.

### e) *General Comment*

The accumulated data in this study show that a mixture of acetonitrile and dimethylsulphoxide is certainly a nonideal mixture which exhibits deviations in practically all the physical properties investigated in this work.

This behaviour is in fact not restricted to the MeCN-DMSO mixtures but extends throughout all polar-solvent mixture systems.

Nonideality arises from molecular interactions in which a solvent molecule acts as a donor (in the Lewis sense) while the other solvent acts as an acceptor.

The acceptor number of DMSO and MeCN is identical (19.3) but the donor numbers are different (29.8 & 14.1) respectively (Gutmann 1978). This difference in the donor numbers would make one act as donor and the other as acceptor which invites donor-acceptor interactions, characterised by new structural features which are absent in either of the solvents.

An extension of the present work may prove of importance not only for academic reasons but for many industrial processes in which mixed polar solvents are being used.

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## دراسة التأثير المتبادل للمذيبات في مخاليط الأسيتونيتريل والداى مثيل سلفوكسيد

سلامة بطرس سلامة، داود دياب وسعد واصف  
قسم الكيمياء - كلية العلوم - جامعة الخرطوم - الخرطوم - السودان

تم تعيين كل من معامل الانكسار، ثوابت العازل، الكثافة،  
الضغط البخارى واللزوجة لمخاليط مختلفة من الاسيتونيتريل  
و الداى مثيل سلفوكسيد .

وقد اوضحت النتائج أن هناك حيوداً عن المثالية يؤكد  
وجود ترابط بين المذيبين .

يصل هذا الترابط إلى مداه عندما تكون النسبة  
الجزيئية بين المذيبين ١ : ١ .

وقد تم إثبات ذلك باستخدام طيف الأشعة تحت  
الحمراء وطيف رامان .