

Chemistry

LIQUID–VAPOR EQUILIBRIUM  
OF DIMETHYL SULFOXIDE–ACETONITRILE SYSTEM  
AT THE TEMPERATURE RANGE 293.15–323.15 K

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The liquid–vapor phase equilibrium in the dimethyl sulfoxide–acetonitrile binary system was studied using a static method. The total saturated vapor pressure at the temperature range 293.15–323.15 K is measured. Partial pressures of dimethyl sulfoxide and acetonitrile were calculated by integrating the Gibbs–Duhem equation. Molar excess Gibbs energies were described by the Redlich–Kister equation, and correlation parameters were calculated. It was found that molar excess Gibbs energies are negative, and the deviation from ideality increases as temperature increases.

**Keywords:** dimethyl sulfoxide, acetonitrile, saturated vapor pressure, partial pressure, excess molar Gibbs energy.

**Introduction.** The biomedical and theoretical significance for fundamental investigations of dimethyl sulfoxide (DMSO)–acetonitrile (ACN) binary system arises from several reasons. DMSO and ACN belong to the organic solvents, which are widely used in chemistry, biochemistry, pharmacy and many branches of industry [1, 2]. Moreover, the DMSO–ACN system is interesting, because its components composed of molecules with the same dipole moment value (about 4 D), show many striking differences in their physical properties. Although ACN is referred, by many authors, as the “leading dipolar system”, where strong dipole–dipole coupling determines most of its physical properties [3], at the same time, DMSO exhibits really exceptional and unexpected properties.

In this work on the basis of liquid–vapor phase equilibrium experimental data of pure liquids (DMSO, ACN) and their binary mixture, the molar enthalpies and entropies of vaporization, partial pressures and excess molar Gibbs energies have been calculated.

**Materials and Methods.** DMSO (“Aldrich”, 99.5%, without further purification) and ACN (with 99.9% purity) were used.

Saturated vapor pressure was measured via the static method using mercury and oil pressure gauges, as described in [4, 5]. The vapor pressure of pure DMSO was determined using an oil gauge; this parameter of pure ACN and the solutions were measured with mercury gauges. VM-1 diffusion oil with a density of  $0.863 \text{ g}\cdot\text{cm}^{-3}$

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was used in the oil pressure gauge (15.7 mm of the oil column corresponded to 1 mm Hg; i.e. 1 mm of the oil column corresponded to 8.494 Pa). The studied liquid was thermostatically controlled during the measurements. The temperature was controlled using a contact thermometer and measured using a mercury laboratory thermometer with a scale interval of 0.1°C. The time of measuring pressure at each temperature was 10 min.

**Results and Discussion.** Saturated vapor pressure was measured above both pure substances (DMSO, ACN) and DMSO–ACN binary solutions over the range of concentrations at 293.15 and 323.15 K temperatures.

The molar enthalpies of vaporization of these substances were calculated from the resulting data on the saturated vapor pressure (Tab. 1) of the pure substances and the dependence of  $\ln P$  on the reciprocal of the temperature, described by the Clapeyron–Clausius equation (Tab. 2), the results are in good agreement with the data of [6, 7].

Table 1

*Saturated vapor pressures of DMSO and ACN (P, Pa) at different temperatures*

<i>T, K</i>	DMSO	ACN
293.15	51	10666
298.15	75	12266
303.15	113	15065
308.15	145	18532
313.15	214	23331
318.15	303	28264
323.15	406	34397

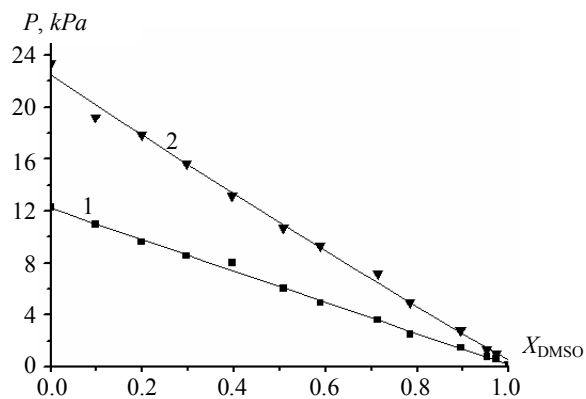
The ebullioscopic constants and the changes in entropy during vaporization for both pure substances were calculated as well (Tab. 2). It is known that for non associated liquids the change in entropy during the vaporization of one mole of a substance is  $\sim 88 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  (Trouton's constant). The considerable positive deviation from this value suggests that the molecules of these liquids were strongly associated.

Table 2

*Molar enthalpies ( $\Delta_v H$ ) and entropies of vaporization ( $\Delta_v S$ ) and ebullioscopic constants ( $K_{eb}$ ) of pure DMSO and ACN*

Substance	$\Delta_v H, \text{kJ}\cdot\text{mol}^{-1}$	$\Delta_v S, \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$K_{eb}, \text{K}\cdot\text{kg}\cdot\text{mol}^{-1}$
DMSO	53.86	117	2.57
ACN	33.67	95	1.27

The total saturated vapor pressures above DMSO–ACN solutions with compositions of the entire concentration range at temperatures of 293.15–323.15 K were measured as well. The experimental data of saturated vapor total pressure for 298.15 and 313.15 K are reported in Tab. 3. The data show, that the total vapor pressure of the solutions rose along with temperature and the decreasing mole fraction of DMSO. The dependence of the total pressure on the mole fraction of DMSO in the DMSO–ACN solutions at 298.15 and 313.15 K is shown in Figure.



Dependences of the total saturated vapor pressure of DMSO-acetonitrile solutions on the mole fraction of DMSO at:  
1 – 298.15 K;  
2 – 313.15 K.

Table 3

Total ( $P$ ) and partial ( $P_{\text{DMSO}}$ ,  $P_{\text{ACN}}$ ) saturated vapor pressures and excess molar Gibbs energies ( $G^E$ ) of DMSO-ACN solutions at 298.15 and 313.15 K

$T, K$	$X_{\text{DMSO}}$	$P, Pa$	$P_{\text{DMSO}}, Pa$	$P_{\text{ACN}}, Pa$	$G^E, J \cdot mol^{-1}$
298.15	0.0000	12266	0	12266	0
	0.0980	10932	5	10927	-297
	0.1988	9599	12	9587	-391
	0.2966	8533	18	8515	-368
	0.3959	7999	24	7975	-297
	0.5078	5999	31	5968	-218
	0.5887	4933	36	4897	-182
	0.7138	3600	45	3555	-164
	0.7848	2533	49	2484	-163
	0.8946	1467	58	1408	-131
	0.9526	767	63	704	-77
	0.9724	581	66	515	-49
1.0000	75	75	0	0	
313.15	0.0000	23331	0	23331	0
	0.0980	19198	16	19183	-462
	0.1988	17865	32	17833	-576
	0.2966	15599	49	15550	-506
	0.3959	13199	67	13131	-382
	0.5078	10666	87	10579	-280
	0.5887	9333	101	9231	-261
	0.7138	7199	123	7076	-308
	0.7848	4933	137	4796	-341
	0.8946	2800	155	2645	-301
	0.9526	1336	163	1173	-181
	0.9724	1008	166	842	-116
	1.0000	214	214	0	0

The partial saturated vapor pressures of the individual components were calculated by integrating the Gibbs–Duhem equation:

$$\ln P_{\text{DMSO}} = \ln P_{\text{DMSO}}^0 - \int_0^{X_{\text{ACN}}} (X_{\text{ACN}} / X_{\text{DMSO}}) d \ln P_{\text{ACN}}, \quad (1)$$

where  $P_{\text{DMSO}}$  is the partial pressure of DMSO,  $P_{\text{ACN}}$  is the partial pressure of ACN,  $P_{\text{DMSO}}^0$  is the vapor pressure of pure DMSO,  $X_{\text{DMSO}}$  is the mole fraction of DMSO, and  $X_{\text{ACN}}$  is the mole fraction of ACN in the binary solution. The integrated portion of Eq. (1) was determined graphically. The partial pressures of the solution components were calculated as described in [4, 5]. The calculated partial pressures and excess molar Gibbs energies are listed in Tab. 3. The data on excess molar Gibbs energy were correlated using the Redlich–Kister equation [5, 8]:

$$G^E = RT X_{\text{DMSO}} X_{\text{ACN}} \left[ B + C(2X_{\text{DMSO}} - 1) + D(2X_{\text{DMSO}} - 1)^2 \right]. \quad (2)$$

Correlation coefficients  $B$ ,  $C$ , and  $D$  were calculated using the Origin 7.5 software package. Standard deviations ( $\sigma$ ) of the calculated and experimental values were estimated as follows:

$$\sigma = \left[ \sum_{i=1}^n (G_{i,\text{exp}}^E - G_{i,\text{calc}}^E)^2 / (m - n) \right]^{1/2}, \quad (3)$$

where  $m$  is the volume of experimental data and  $n$  is the number of parameters. The values of the parameters of the Redlich–Kister equation (correlation coefficients  $B$ ,  $C$  and  $D$ ) and standard deviations ( $\sigma$ ) are listed in Tab. 4.

*Table 4*

*Parameters of the Redlich–Kister equation ( $B$ ,  $C$ , and  $D$ ) and standard deviations ( $\sigma$ )*

$T, K$	$B$	$C$	$D$	$\sigma$
298.15	-0.3597	0.4834	-0.9382	186
313.15	-0.4373	0.4619	-1.8549	240

It is known that excess molar thermodynamic characteristics, particularly excess molar Gibbs energy, are quite helpful in estimating intermolecular interactions in solutions. It is also known that negative values of excess molar quantities suggest that the molecules of the components undergo strong intermolecular interactions. As it follows from data, the excess molar Gibbs energies are negative and their dependences on composition exhibit extreme behavior. We believe that hetero-association in this case occurs due to the formation of dipole-dipole coupling between molecules of DMSO and ACN, which is in good agreement with [9].

Our data suggest that an increase in temperature generally leads to a change in the dependence of the excess molar Gibbs energy on the mole fraction of DMSO in solutions. The obtained data assume that an increase in the temperature in a DMSO–ACN solution leads to the enhanced degradation of homoassociates, and to the dominant formation of hetero-associates by dipole-dipole interaction.

**Conclusion.** Our results from studying liquid–vapor phase equilibrium in DMSO–ACN binary systems revealed the formation of dipole-dipole coupling between molecules of DMSO and ACN, which is evident from the negative value of the excess molar Gibbs energies.

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