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Thermodynamics of Liquid–Vapor Phase Equilibrium in Dimethyl Sulfoxide–Alkanol Systems in the Range of 293.15–323.15 K

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Abstract—Liquid–vapor phase equilibria in dimethyl sulfoxide–alkanol (1-propanol, 1-butanol, and *tert*-butanol) binary systems are studied using a static method. The total saturated vapor pressure in the temperature range of 293.15–323.15 K is measured. The partial pressures of dimethyl sulfoxide and alkanes have been calculated via integrating the Gibbs–Duhem equation. Excess molar Gibbs energies are described by the Redlich–Kister equation, and the correlation parameters are calculated. The nature of the deviation from the ideal behavior of these solutions is explained by allowing for the presence of competing homo- and heteromolecular interactions and the considerable effect of the length of the alkanols' hydrocarbon chains has on the values of the thermodynamic parameters.

Keywords: dimethyl sulfoxide, alkanol, saturated vapor pressure, partial pressure, excess Gibbs energy.

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INTRODUCTION

Studying the liquid–vapor phase equilibria of binary systems is an important problem in the physical chemistry of solutions. The pressure of saturated vapors that are in equilibrium with a liquid depends on the nature and temperature of the liquid and provides information on intermolecular interactions. The practical importance of research into the liquid–vapor phase equilibria of alcohol solutions of dimethyl sulfoxide (DMSO) is associated with the biomedical importance of the components [1–3]. In addition, DMSO–alkanol (ROH) solutions are of interest because the solution components are capable of both self-association and forming heteroassociates with hydrogen bonds [4–9]. It is obvious that the presence of these competing interactions has a substantial effect on the liquid–vapor equilibria in such solutions.

This work is a continuation of our research into the liquid–vapor phase equilibria of solutions of DMSO with saturated monohydric alcohols (methanol and ethanol) [4, 5]. The liquid–vapor phase equilibria in binary solutions of DMSO with representatives of alkanols—1-propanol, 1-butanol, and *tert*-butanol—are studied. The results from measuring the total saturated vapor pressure of these binary systems in the temperature range of 293.15–323.15 K are described. The partial pressures of the individual components, the excess molar Gibbs energies, and the correlation parameters are calculated.

EXPERIMENTAL

DMSO (Aldrich Chemical, 99.5%, without further purification) and distilled alcohols (1-propanol, 1-butanol, and *tert*-butanol) with 99.9% purity were used in this work.

Saturated vapor pressure was measured via the static method using mercury and oil pressure gauges, as described in [10, 11]. The vapor pressure of pure DMSO was determined using an oil gauge; this parameter of pure alcohol and the solutions was measured with mercury gauges. VM-1 diffusion oil with a density of 0.863 g cm⁻³ was used in the oil pressure gauge (15.7 mm of the oil column corresponded to 1 mmHg; i.e., 1 mm of the oil column corresponded to 8.494 Pa). The studied liquid was thermostatically controlled during 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, 1-propanol, 1-butanol, and *tert*-butanol) and DMSO–alkanol binary solutions over the range of concentrations at temperatures of 293.15–323.15 K. The molar enthalpies of vaporization of these substances were calculated from the resulting data on the saturated vapor pressure of the pure substances (Table 1) and the dependence of $\ln P$

Table 1. Saturated vapor pressures of DMSO, 1-propanol, 1-butanol, and *tert*-butanol at different temperatures, kPa

<i>T</i> , K	DMSO	Methanol	Ethanol	1-Propanol	1-Butanol	<i>tert</i> -Butanol
293.15	0.051	12.932	5.733	2.266	0.667	4.266
298.15	0.075	16.666	7.999	3.333	0.800	5.999
303.15	0.113	21.599	10.266	4.666	1.200	8.133
308.15	0.145	27.598	13.599	6.133	1.733	10.932
313.15	0.214	35.464	17.865	8.133	2.533	14.532
318.15	0.303	46.663	22.665	10.546	3.466	19.198
323.15	0.406	53.330	29.331	13.865	4.533	25.198

The data on methanol and ethanol are taken from [4] and [5], respectively.

on the reciprocal of the temperature, described by the Clapeyron–Clausius equation (Table 2); the results are in good agreement with the data of [12–14]. In addition, we calculated the ebullioscopic constants and the changes in entropy during vaporization (Table 2). For comparison, Table 1 lists the data on methanol and ethanol taken from [4, 5]. It is known that for non-associated liquids, the change in entropy during the vaporization of one mole of a substance is ~ 88 J/(mol K) (Trouton's constant). The considerable positive deviation from this value suggests that the molecules of the studied alkanols (1-propanol, 1-butanol, and *tert*-butanol) were strongly associated, as were methanol and ethanol in [4, 5] and DMSO in [4].

In addition, the total saturated vapor pressures above DMSO–ROH solutions with compositions of the entire concentration range at temperatures of 293.15–323.15 K were measured. The data in Table 3 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–alkanol solutions at 298.15 K is shown in Fig. 1. It is evident from the experimental data that the negative deviation from ideality diminished upon an increase in the length of the hydrocarbon chains.

Table 2. Molar enthalpies ($\Delta_v H$) and entropies of vaporization ($\Delta_v S$) and ebullioscopic constants (K_{eb}) of pure alkanols

Substance	$\Delta_v H$, kJ/mol	$\Delta_v S$, J/(mol K)	K_{eb} , K kg/mol
1-Propanol	46.17 ± 0.71 (47.5 ± 0.4) [12]	121	1.57
1-Butanol	52.98 ± 1.9 (52.42 ± 2.3) [12] (52.34 ± 0.03) [13]	132	1.87
<i>tert</i> -Butanol	46.48 ± 0.25 (46.12 ± 0.05) [14]	127	1.77

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

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

where P_{DMSO} is the partial pressure of DMSO, P_{ROH} is the partial pressure of alcohols, P_{DMSO}° is the vapor pressure of pure DMSO, X_{DMSO} is the mole fraction of DMSO, and X_{ROH} is the mole fraction of alcohols in the binary solution. The integrated portion of Eq. (1) was determined graphically. The partial pressures of the solution components were calculated as described

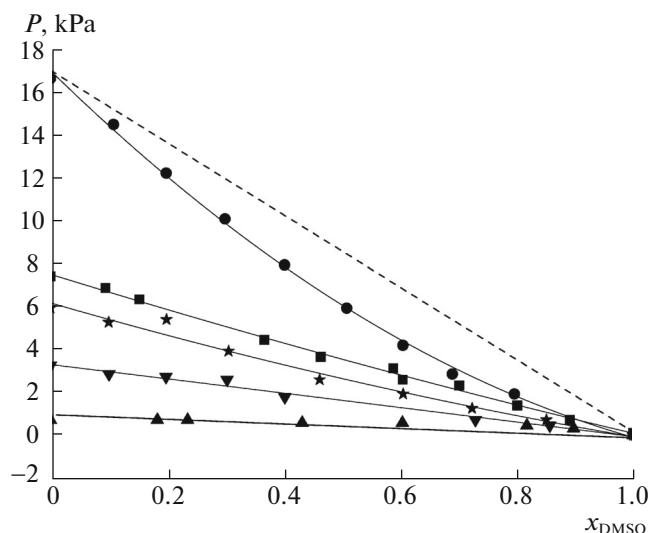
**Fig. 1.** Dependences of the total saturated vapor pressure of DMSO–alkanol solutions on the mole fraction of DMSO at 298.15 K: (●) DMSO + methanol [4], (■) DMSO + ethanol [5], (▼) DMSO + 1-propanol, (▲) DMSO + 1-butanol, and (★) DMSO + *tert*-butanol.

Table 3. Total (P) and partial saturated vapor pressures (P_{DMSO} ; P_{ROH}) and excess molar Gibbs energies (G^E) of DMSO–alkanol solutions at different temperatures

T , K	X_{DMSO}	P_{tot} , Pa	P_{DMSO} , Pa	P_{ROH} , Pa	G^E , J/mol	T , K	X_{DMSO}	P_{tot} , Pa	P_{DMSO} , Pa	P_{ROH} , Pa	G^E , J/mol
DMSO + 1-propanol						DMSO + 1-butanol					
293.15	0.0000	2267	0	2267	0	308.15	0.0000	1733	0	1733	0
	0.1984	1999	3	1997	−449		0.1836	1733	24	1710	337
	0.4023	1467	6	1461	−1178		0.4319	1200	79	1121	441
	0.7294	534	22	512	−1078		0.8176	1067	93	974	8
	1.0000	51	51	0	0		1.0000	145	145	0	0
298.15	0.0000	333	0	3333	0	323.15	0.0000	4533	0	4533	0
	0.1984	279	5	2794	−402		0.1836	4266	44	4222	33
	0.4023	1867	26	1841	−268		0.4319	2800	158	2641	−80
	0.7294	800	47	753	−387		0.8176	1733	245	1488	−381
	1.0000	75	75	0	0		1.0000	406	406	0	0
308.15	0.0000	6133	0	6133	0	DMSO + <i>tert</i> -butanol					
	0.1984	4533	10	4523	−706	293.15	0.0000	4266	0	4266	0
	0.4023	2800	32	2767	−104		0.1992	3333	4	3329	−465
	0.7294	1467	63	1404	−109		0.4619	2000	14	1986	−792
	1.0000	145	14	0	0		0.7236	800	25	775	−968
0.0000	13865	0	13865	0	1.0000		51	51	0	0	
323.15	0.0000	9999	23	9976	−898	298.15	0.0000	5999	0	5999	0
	0.1984	6933	62	6871	−1352		0.1992	5466	4	5462	−389
	0.4023	2852	150	2703	−1575		0.4619	2666	23	2644	−745
	0.7294	406	406	0	0		0.7236	1333	37	1296	−832
	1.0000	406	406	0	0		1.0000	75	75	0	0
DMSO + 1-butanol						308.15	0.0000	10932	0	10932	0
293.1	0.0000	667	0	667	0		0.1992	8133	12	8120	−590
	0.1836	533	27	506	333		0.4619	4800	45	4755	−773
	0.4319	533	29	504	688		0.7236	2266	78	2188	−776
	0.8176	400	34	366	98		1.0000	145	145	0	0
	1.0000	51	51	0	0	0.0000	25198	0	25198	0	
298.15	0.0000	800	0	800	0	323.15	0.0000	19065	31	19034	−641
	0.1836	800	28	772	658		0.1992	10799	125	10674	−846
	0.4319	667	45	621	804		0.4619	5333	216	5117	−828
	0.8176	533	52	481	228		0.7236	406	406	0	0
	1.0000	75	75	0	0		1.0000	406	406	0	0

in [10, 11]. The calculated partial pressures are listed in Table 3.

The experimental data were also used to calculate the excess molar Gibbs energies (G^E) (Table 3). The data on excess molar Gibbs energy were correlated using the Redlich–Kister equation [4, 5]:

$$G^E = RTx_{\text{DMSO}}x_{\text{ROH}} \times [B + C(2x_{\text{DMSO}} - 1) + D(2x_{\text{DMSO}} - 1)^2]. \quad (2)$$

Correlation coefficients B , C , and D were calculated using the Origin 7.5 software package. Standard deviations (σ) 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 parame-

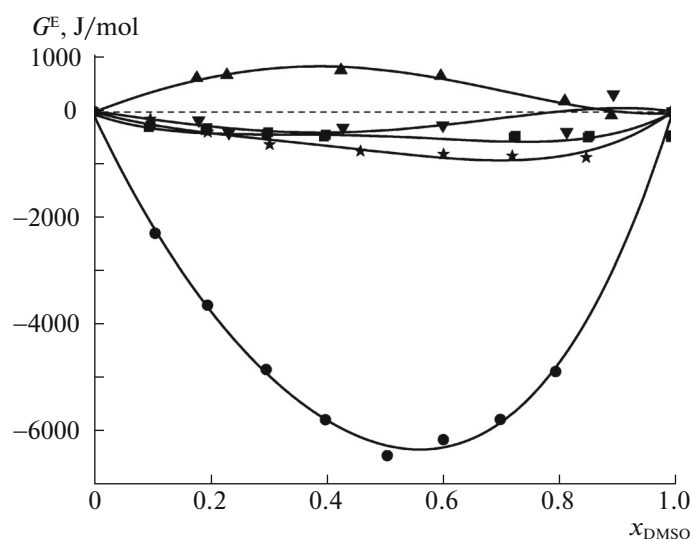
Table 4. Parameters of the Redlich–Kister equation (B , C , and D) and standard deviations (σ)

T , K	B	C	D	σ
DMSO + 1-propanol				
293.15	-2.0745	-1.3278	-0.1269	152.61
298.15	-0.5811	0.5670	0.5871	198.91
303.15	-1.7618	-1.2948	-1.7053	118.72
308.15	-1.7031	-0.8313	-1.7153	101.25
313.15	-1.4670	-0.4689	-1.4419	93.02
318.15	-1.8734	-1.1596	-2.2052	130.48
323.15	-2.1628	-1.3773	-2.3305	153.83
DMSO + 1-butanol				
293.15	1.1461	-0.6246	-1.5920	46.68
298.15	1.3103	-0.9223	-0.5958	60.82
303.15	0.9122	-0.6063	-0.8446	92.98
308.15	0.7735	-0.6972	-1.3424	100.15
313.15	0.3493	-0.4709	-1.6298	109.39
318.15	0.0510	-0.2999	-1.4344	105.81
323.15	-0.0709	-0.8832	-1.4579	111.95
DMSO + <i>tert</i> -butanol				
293.15	-1.3465	-1.1175	-1.4631	64.62
298.15	-1.2232	-0.9431	-0.9790	93.75
303.15	-1.4750	-0.7671	-1.6248	83.35
308.15	-1.1869	-0.5211	-1.4924	92.47
313.15	-1.1890	-0.7522	-1.5018	93.91
318.15	-1.5602	-1.0632	-2.2781	139.36
323.15	-1.5361	-1.0467	-2.2428	230.40

ters of the Redlich–Kister equation (correlation coefficients B , C , and D) and standard deviations (σ) are listed in Table 4.

The plotted dependence of the excess Gibbs energy on the mole fraction of DMSO in the solutions at 298.15 K is shown in Fig. 2. For comparison, the figure also shows the data on G^E previously obtained for DMSO–methanol (ethanol) binary solutions at the same temperature [4, 5]. 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. It is evident from Fig. 2 that in all cases except for DMSO–1-butanol solutions, the excess molar Gibbs energies are negative and their dependences on composition exhibit extreme behavior. Heteroassociation in this case occurs due to the formation of hydrogen bonds. The greatest negative deviations are observed for compositions with $X_{\text{DMSO}} \approx 0.4\text{--}0.7$; so the formation of DMSO–alcohol heteroassociates dominates in this range of concentrations.

The positive Gibbs energy in DMSO–1-butanol solutions indicates the occurrence of interactions that compete with hydrogen bonds. It is assumed that upon an increase in molecular weight and the length of alcohol hydrocarbon chains, the strength of dispersion forces (i.e., hydrophobic interactions) is enhanced and contributes to the competition between homo- and heteroassociates. This assumption is confirmed by the the excess molar Gibbs energies being negative in the case of *tert*-butanol. The London dispersion forces of *tert*-butanol are in fact weaker than those of their iso-

**Fig. 2.** Dependences of the excess molar Gibbs energy on the mole fraction of DMSO in the DMSO–alcohol binary systems at 298.15 K; the symbols are the same as in Fig. 1.

mer (i.e., 1-butanol). In accordance with the theory of hydrophobic effects [15], the surface of contact for hydrophobic interactions is smaller and the heteroassociates formed by intermolecular hydrogen bonds dominate in a DMSO–*tert*-butanol solution, due to the branched structure of *tert*-butanol. This explanation is in fact in good agreement with the results from research into the bulk properties of DMSO solutions with certain primary and secondary alkanols [6, 9].

Table 3 lists the excess molar Gibbs energies at different temperatures. Our data suggest that an increase in temperature generally does not lead to a change in the dependence of the excess molar Gibbs energy on the mole fraction of DMSO in solutions. The effect of temperature is clearly pronounced in concentrated DMSO–1-butanol solutions, where an increase in temperature results in a change not only in the magnitude, but also in the nature of the deviation from ideality: from positive to negative. We may assume that an increase in the temperature in a DMSO–1-butanol solution leads to the enhanced degradation of homoassociates, and to the dominant formation of heteroassociates.

CONCLUSIONS

Our results from studying liquid–vapor phase equilibria in DMSO–alkanol binary systems revealed the formation of hydrogen bonds between molecules of DMSO and alkanols, which is evident from the negative value of the excess molar Gibbs energies. It was found that the length of alcohol hydrocarbon chains has a considerable effect on the values of excess thermodynamic parameters.

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