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DETERMINATION OF THE INTERMOLECULAR INTERACTION PARAMETERS IN THE WATER–AMIDE SYSTEMS BASED ON THE DATA OF THE EXCESS THERMODYNAMIC FUNCTIONS

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Abstract

The molar excess enthalpies H^E for the water +N-methyl-2-pyrrolidinone binary mixtures have been measured as functions of mole fraction at 298.15, 308.15 and 318.15 K, using isoperibol rotating calorimeter. A hydrogen bonding pairs model proposed by Luzar was fitted to the experimental data H^E, G^E for the binary mixtures of water with hexamethylphosphoric triamide, N,N-dimethylformamide, N,N-dimethylacetamide and N-methyl-2-pyrrolidinone.

Keywords: excess thermodynamic functions of mixing, water+amide mixtures

Introduction

The intermolecular interaction in water–aprotic amide binary systems attracts the attention of many authors [1, 2]. Excess thermodynamic functions are very important for understanding specificity of those interactions. This investigation is part of our studies on the thermodynamic properties of binary mixtures consisting of some amides and water. We have recently reported excess thermodynamic functions (H^E, G^E, TS^E) for the binary mixtures of water with hexamethylphosphoric triamide (HMPT), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA) at 298.15, 308.15 and 318.15 K [3–5].

In this paper we present the excess molar enthalpy of water with N-methyl-2-pyrrolidinone (MP) at the same temperatures. Values of excess molar Gibbs function of this system at 298.15 K were calculated using the activity coefficients of components [6]. The volumetric and the thermochemical data indicate the strong intermolecular interactions and the formation of hydrogen-bonded complexes in all these mixtures [1–5, 7]. However, available estimations of hydrogen bonds strength and associates' compositions in the water–amide systems are very contradictory [8–10].

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A simple hydrogen-bonding pairs model worked out by Luzar [11] was applied to calculate energy (E) and entropy (ΔS) of formation of hydrogen bonds between water molecules and amide oxygen and to evaluate the contributions of these bonds in the total values of excess thermodynamic functions of mixing.

Experimental

N-methyl-2-pyrrolidinone of 'pure' classification was refluxed over CaH_2 and then distilled at reduced pressure. The refined solvent was dried and then stored over 4A molecular sieves. The water content determined according to Fisher's method was less then 0.02 mass.%. We used water twice distilled in glass apparatus. Excess molar enthalpies were measured over the whole composition range using an isoperibol calorimeter with original system of rotation calorimetric vessel [12]. The experimental procedure and a test of calorimetric system have been reported elsewhere [13]. The uncertainty in the determination of enthalpies is estimated to be less than 1%.

Results and discussion

The experimental H^E results for the binary system water–MP at different temperatures are presented in Table 1. To the excess enthalpies we fitted the equation:

$$H^E(\text{J}\cdot\text{mol}^{-1}) = x_1x_2 \sum_{n=1}^{p} C_n(x_1 - x_2)^{n-1} \tag{1}$$

The constants C_i and standard errors are given in Table 1; x_1 and x_2 are the mole fractions of the components. In the present work, the compositions of the mixtures are stated in terms of the mole fraction x_i of the components. The subscripts 1 and 2 designate water and amides (DMF, MP, DMA, HMPT), respectively. Our results for the system water–MP at 298.15 K are in good agreement with those of Murakami *et al.* [14].

The Luzar model treats water–aprotic solvent mixture as an assembly of hydrogen bonding pairs. Each pair consists of proton of water molecule and a lone electron pair of the oxygen atom in water or in organic component molecule. In our case, according to this model, the molecules of amide are capable to form hydrogen bonds with two or three molecules of water (m) taking into account intramolecular electron effects. The calculated excess molar enthalpy and excess Gibbs energy curves for water–amide systems at 298.15 K are plotted in Fig. 1, together with the curves representing experimental results smoothed by Eq. (1). All these systems belong to the class of typically non-aqueous mixtures

(TNAN) [15]. Parameters of hydrogen bonds and fraction of formed bonds ω in water–amide systems are presented in Table 2. We carried out the model calculations by means of the program that had been tested by water–DMSO system.

Table 1 Experimental results of molar excess enthalpies H^E of water+N-methyl-2-pyrrolidinone mixtures (MP), x_2 – mole fraction of MP, s – standard error

χ_2	$-H^E$ / J·mol^{-1}	χ_2	$-H^E$ / J·mol^{-1}	χ_2	$-H^E$ / J·mol^{-1}
		T=298.15 K			
0.0020	42.31	0.0635	1154	0.4005	2742
0.0040	84.14	0.1122	1803	0.4508	2613
0.0060	125.8	0.1505	2189	0.5522	2229
0.0080	167.1	0.2002	2538	0.6532	1758
0.0100	207.6	0.2501	2742	0.7508	1251
0.0150	306.6	0.3003	2830	0.8501	739.4
0.0200	405.0	0.3335	2835	0.9500	239.4
0.0414	795.5				
C_1=–9758.91	C_2=–7695.06	C_3=–3840.26	C_4=–748.01	C_5=745.13	s=3.9
		T=308.15 K			
0.0020	39.52	0.0603	1050	0.4017	2597
0.0040	78.70	0.1121	1701	0.4513	2473
0.0060	117.6	0.1509	2071	0.5521	2109
0.0080	156.4	0.2005	2406	0.6559	1647
0.0100	194.9	0.2514	2603	0.7510	1189
0.0150	288.8	0.3026	2683	0.8501	708.7
0.0195	372.0	0.3355	2686	0.9650	160.6
0.0404	740.0				
C_1=–9237.54	C_2=–7224.57	C_3=–3682.32	C_4=–543.08	C_5=680.93	s=3.1
		T=318.15 K			
0.0020	36.88	0.0604	981.9	0.4029	2462
0.0040	73.60	0.1116	1594	0.4516	2348
0.0060	110.1	0.1510	1952	0.5501	2014
0.0080	146.3	0.2002	2267	0.6571	1568
0.0100	182.2	0.2508	2458	0.7510	1142
0.0150	271.1	0.3024	2541	0.8501	678.2
0.0200	358.6	0.3364	2545	0.9549	201.3
0.0409	697.2				
C_1=–8782.70	C_2=–6866.04	C_3=–3487.94	C_4=–406.29	C_5=813.69	s=2.4

The results of our calculations were found to be identical with Luzar data for this system [11].

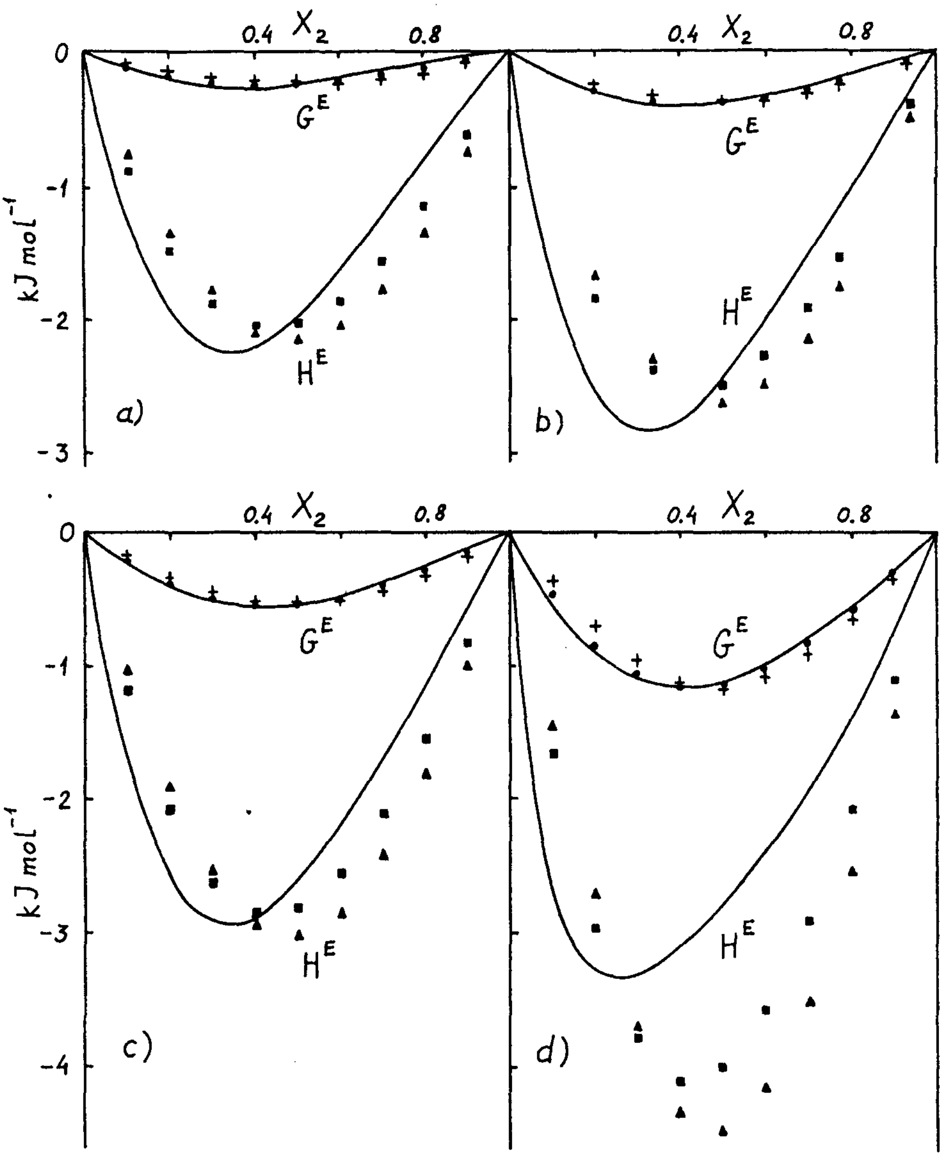

Fig. 1 Excess thermodynamic functions for water–amide systems at 298.15 K: a - water–DMF, b - water–MP, c - water –DMA, d - water–GMPT: —— -calculated from Eq. (1), calculated from Luzar method G^E: •–m=3, +–m=2; H^E: ■–m=3, ▲–m=2

Table 2 Hydrogen bond parameters for water–amide systems at 298.15 K

System	m	$-E$ / kJ·mol^{-1}				ω	$-\Delta S$ / J·mol^{-1}K^{-1}		
		present results	literature values				present results	literature values	
water-DMF	2	17.6	13.4;[a]	14.6;[b]	15.1[c]	0.904	40.6	32.6[a]	
	3	16.8				0.902	37.9		
water-MP	2	18.3		–		0.913	41.9	–	
	3	17.4				0.909	39.0		
water-DMA	2	18.7	13.3;[a]	17.8;[b]	15.9;[c]	0.922	42.1	26.5;[a]	49.8[d]
	3	17.6		15.1[d]		0.918	39.2		
water-HMPT	2	20.1		18.8[e]		0.945	44.0	–	
	3	18.6				0.939	39.7		

[a]Ref. 8, [b]Ref. 9, [c]Ref. 10, [d]Ref. 16, [e]Ref. 1

Quantitative agreement of theoretical values of excess thermodynamic functions with experimental results as well as values E and ΔS with spectroscopic measurements data indicates that hydrogen bond represents the dominant intermolecular interaction in all these systems. The largest difference of the theoretical and experimental data of excess enthalpy is in the water–HMPT system. On the one hand, it is due to the fact that Luzar model doesn't take into account the hydrophobic effects and changes of other possible types of intermolecular interactions. On the other hand, formation of the hydrogen bonds between HMPT and water molecules is restricted by steric constraint [17]. It has been found that water–amide hydrogen bonds are stronger than those between water molecules ($E=-13.4$ kJ·mol^{-1} [11]) and their strength increases with increasing of donor number of amides. The negative values of the enthalpies of mixing appear to be a consequence of the difference in the strength of these hydrogen bonds, rather than a result of any considerable change in the total number of hydrogen bonds in the systems. According to the model the temperature decrease of exothermicity of mixing is connected with the decrease water–amide hydrogen bonds fraction. For example, that fraction falls from 0.922 at 298.15 K to 0.883 at 318.15 K in water–DMA system ($m=2$).

Table 3 Number densities of water–DMA hydrogen bonding paizs (ρ_{12}) and average numbers of hydrogen bonds per water molecule, $<n_{HB}>$, as a function of the mole fraction of DMA, x_2, at 298.15 K ($m=2$)

χ_2	ρ_1/	ρ_2/	ρ_{12}/	$< n_{HB}^{11} >$	$< n_{HB}^{12} >$	$< n_{HB} >$
		mol·cm^{-3}				
0	0.0553	0.	0.	1.77	0.	1.77
0.2	0.0252	0.0063	0.0112	1.38	0.41	1.79
0.4	0.0131	0.0087	0.0119	0.97	0.84	1.81
0.5	0.0094	0.0094	0.0106	0.77	1.04	1.81
0.6	0.0066	0.0099	0.0088	0.59	1.23	1.82
0.8	0.0026	0.0105	0.0044	0.27	1.57	1.84
0.9	0.0012	0.0106	0.0022	0.13	1.71	1.84
1	0.	0.0108	0.	0.	1.84	1.84

The dependencies of number densities of water (ρ_1), DMA (ρ_2) molecules and hydrogen bonding water–DMA pairs (ρ_{12}) on the mixture composition are listed in the left part of Table 3. The analogous results are obtained for the other systems. The data of Table 3 show that the structure of associates changes from DMA·2H_2O to H_2O·2DMA with increasing of DMA concentration. This result is in good agreement with data [17, 18], but contradicts calculations carried out by ideal associated solution model [19, 20]. The average numbers of hydrogen bonds per water molecule for water–water pairs $<n_{HB}^{11}>$, for water–DMA pairs $<n_{HB}^{12}>$ and average total numbers of hydrogen bonds per water molecule in solution $<n_{HB}>$ are listed in the right part of Table 3. It can be seen that at $x_2>0.5$ the probability of water–water hydrogen bond formation is less than 0.4 ($<n_{HB}^{11}>/2$) and therefore the single water hydrogen bond subnetwork splits into small clusters [21]. Table 3 also shows the existence of a considerable number of hydrogen bonds between water molecules at $x_2=0.9$. It is doubtful because of the presence of the abundance of such strong proton acceptor as DMA.

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Zusammenfassung — Unter Anwendung eines isothermischen Rotationskalorimeters wurden die molaren Überschußenthalpien H^E für binäre Gemische aus Wasser+N-Methyl-2-pyrrolidinon als eine Funktion des Molenbruches bei 298.15 und 318.15 K ermittelt. Das von Luzar empfohlene Wasserstoffbindungspaar-Modell wurde an die experimentellen Daten H^E und G^E für die binären Gemische aus Wasser und Hexamethylphosphortriamid, N,N-Dimethylformamid, N,N-Dimethylacetamid und N-Methyl-2-pyrrolidinon angepaßt.