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THERMODYNAMICS OF BUTADIENE-1,3 DISSOLUTION PROCESSES IN AQUEOUS-AMMONIA SOLUTIONS

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Abstract. *The article deals with thermodynamics of butadiene-1,3 dissolution in aqueous-ammonia solutions of potassium nitrate at the temperature range of 20-80 ^{0}C. Based on the data obtained we found that the solubility of butadiene-1,3 in aqueous-ammonia solutions follows the Henry's law. The potassium nitrate has a desalinizing effect on the solubility of butadiene-1,3 which decreases with increasing temperature. The addition of ammonia to water and aqueous solutions of potassium nitrate increases the solubility of butadiene-1,3. We have determined the thermodynamic functions of the dissolution process of butadiene-1,3, and the thermodynamic characteristics of the hydrated hydrocarbon in aqueous-ammonia solutions of potassium nitrate. The increase of dissolution heat of butadiene-1,3 in aqueous ammonia solution of potassium nitrate confirms the assumption of hydrogen bonding between hydrogen atoms of ammonia molecule and π-electrons of butadiene-1,3. Comparison of the numerical values of thermodynamic functions of butadiene-1,3 and 2-methylpropene dissolution process showed that both enthalpy and entropy changes increase with increasing degree of unsaturation of the molecule.*

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Introduction

Aqueous solutions of hydrocarbon gases are widely used in the petrochemical industry. In this connection the study of solubility of these compounds in water and aqueous electrolyte solutions is of great practical importance. Study of ammonia influence on dissolubility of hydrocarbons in aqueous solutions and thermodynamics of these processes acquires special theoretical importance for explanation of peculiarities of nonpolar gas solutions properties and understanding of structural changes of water and its role in biologically important objects.

Study of complexation reactions of silver (I) and copper (I) ions with unsaturated hydrocarbons and ammonia [1] required research of thermodynamics of butadiene-1,3 dissolution in aqueous and aqueous-ammonia solutions of electrolytes. This paper determines

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thermodynamic functions of dissolution process and thermodynamic characteristics of butadiene-1,3 in aqueous and aqueous-ammonia solutions of potassium nitrate.

Main body

We determined the solubility of butadiene-1,3 in a 0.1 M potassium nitrate solution at ammonia molar concentrations of 10^{-4}-10^{-1} mol/L at a temperature range of 20-80 ^{0}C and a hydrocarbon pressure of 386-743 mm Hg.

We determined the solubility of butadiene-1,3 in input-ammonia solutions by gas-liquid chromatography. We used butadiene-1,3 with a mass fraction of the main component of 99.6-99.9%. We prepared the solutions in a thermostatically controlled ($\pm$0.1 ^{o}C) glass reactor with a bubbler and a magnetic stirrer in 0.1 M solutions of potassium nitrate in the presence of ammonia. We forced the gas through the test solution at a constant speed for 45-50 min until an equilibrium state was reached, which was determined by the constancy of the hydrocarbon concentration. To prevent loss of ammonia from the reactor, the hydrocarbon was first passed through a flow reactor with a solution of the same composition. The constancy of the ammonia concentration in the solution was monitored by measuring the pH of the solution on a universal pH-meter; 5-7 samples of the solution were taken from the reactor with a syringe after the equilibrium state was reached and analyzed on a laboratory gas chromatograph with thermal conductivity detector. A diatomaceous brick impregnated with triethylene glycol ether and n-butyric acid served as a stationary phase. Hydrogen carrier gas rate was 60-79 ml/min, hydrogen pressure 0.8 ate, detector current 80 mA, column temperature 50 ^{0}C. We have equipped the chromatograph with a special attachment for introducing liquid samples.

We calculated the solubility of hydrocarbon C, % wt.

$$C = \frac{S \cdot K' \cdot 100}{Q \cdot d},$$

where S is peak area, cm^2;

K' is the calibration factor, g/cm^2;

Q is the sample volume, ml;

d is the density of the solution tested, g/cm^3.

To determine the calibration coefficients, a sample of rectified alcohol was added to a test tube, cooled in an ice-salt mixture and a glass ampoule with a sample of hydrocarbon was placed in it. The flask was closed and the ampoule was broken with a special beater. A sample of the obtained solution was then taken using a micro syringe and analyzed in a chromatograph. The calibration factor was calculated from the analysis of 3-5 samples of alcohol solutions with different hydrocarbon contents.

Based on the experimental data obtained it was found that the solubility of butadiene-1,3 in aqueous-ammonia solutions follows the Henry's law. The Sechenov's equation is fulfilled. Experimental data on butadiene-1,3 solubility in aqueous-ammonia solutions of potassium nitrate (Table 1) show reduction of butadiene-1,3 solubility in 0,1 M solutions of potassium nitrate in comparison with ammonium nitrate solutions [2]. This desalting effect in potassium nitrate solutions decreases with increasing temperature.

Table 1. Dissolubility (*S*, % wt.) of butadiene-1.3 in ammonia-water solutions of KNO_3 (0.1 M) at various temperatures (*T*, ^{0}C) and pressures (*P*, mmHg)

T, ^{0}C	Concentration of ammonia, mol/l									
	0		10^{-4}		10^{-3}		10^{-2}		10^{-1}	
	S	*P*	*S*	*P*	*S*	*P*	*S*	*P*	*S*	*P*
20	0.079	732	0.079	733	0.083	735	0.085	734	0.093	733
30	0.061	713	0.061	714	0.061	714	0.065	717	0.068	719
40	0.045	691	0.045	695	0.045	695	0.044	680	0.049	698
50	0.037	660	0.037	661	0.037	661	0.038	660	0.042	660
60	0.029	594	0.029	594	0.028	594	0.029	593	0.030	592
70	0.019	512	0.019	509	0.019	509	0.018	502	0.018	505
80	0.014	400	0.014	400	0.015	429	0.014	424	0.014	386

Non-electrolytes are usually desalinized by most simple salts and salting out by large molecules of organic salts [3-5]. Cases of salting out at the presence of large ions such as ammonium ions are known. In case of 2-methylpropene solubility in water and aqueous solutions of ammonium nitrate this effect is practically not observed.

The addition of ammonia to water and aqueous electrolyte solutions increases the solubility of butadiene-1,3, which is primarily due to the hydrophobic interaction of the hydrocarbon with the ammonia molecules. Reorientation of the water dipoles in the hydrocarbon hydrate shell causes a reorientation of the dipoles in the ammonia hydrate shell. The contribution of the ammonia-water dipole interaction decreases and the contribution of the dispersion interaction increases. The strengthening of the water structure in the hydrate shells of the ammonia and hydrocarbon molecules, leading to a reduction in entropy, causes a hydrophobic hydrocarbon-ammonia interaction. This hydrophobic effect increases with increasing ammonia concentration and is little dependent on the nature of the electrolyte. With increasing temperature, the effect of ammonia on solubility decreases and becomes little noticeable at 40-50 ^{0}C.

It was suggested that hydrogen bonding between hydrogen atoms of ammonia molecule and π-electrons of butadiene-1,3 was formed earlier [2] to explain increased solubility of 1,3-butadiene in aqueous electrolyte solution in the presence of ammonia. This assumption is confirmed by an increase in the dissolution heat of the hydrocarbon in the ammonia-water solution of the electrolyte and a decrease in the suction effect with increasing temperature.

Hydrocarbon gas solutions in water have a number of features that distinguish them from non-aqueous solvents. The solubility of hydrocarbons in water is much lower than in non-polar solvents. The anomalies of aqueous hydrocarbon solutions [6-13] can be explained on the basis of current ideas about the structure of water [14-16]. There is some evidence that a change in temperature leads to a significant restructuring of the structure of water, a change in the near-orderedness of its molecules. The decrease of enthalpy and entropy during dissolution of hydrocarbon gases is related to the shift of equilibrium in solutions towards formation of ice-like crystal structures, formation of cavities in water and with introduction of gas molecules into these cavities. The non-electrolyte displaces water molecules into the crystal framework, resulting in an increase in the number of hydrogen bonds.

The Henry's coefficients were calculated from the experimental data obtained on the solubility of butadiene-1,3 (Table 2).

Table 2. Henry's coefficients ($K\cdot10^{-6}$) (mmHg$\cdot$ mol solution/mol gas) for butadiene-1.3 solutions in water and in 0.1 M aqueous ammonium nitrate solutions at different temperatures

Temperature, ^{0}C		20	30	40	50	60	70	80
Water		2.49	3.25	3.94	4.98	6.01	7.33	8.29
Solution KNO_3								
Concentration of ammonia, mol/l	0	2.74	3.54	4.55	5.29	6.0	7.75	8.6
	0.0001	2.73	3.53	4.54	5.28	6.03	7.73	8.59
	0.001	2.64	3.51	4.53	5.25	6.00	7.72	8.56
	0.01	2.57	3.30	4.51	5.21	6.00	7.77	8.54
	0.1	2.36	3.15	4.28	4.58	5.80	7.78	8.52

As we see from Fig. 1, the dependence of the logarithm of the inverse of the Henry coefficient on the inverse of the temperature is linear. The dissolution heats of the hydrocarbons were calculated from the tangent of the slope of these lines. The values obtained were used to calculate ΔG^o_{298} and ΔS^o_{298} of the hydrocarbon dissolution process.

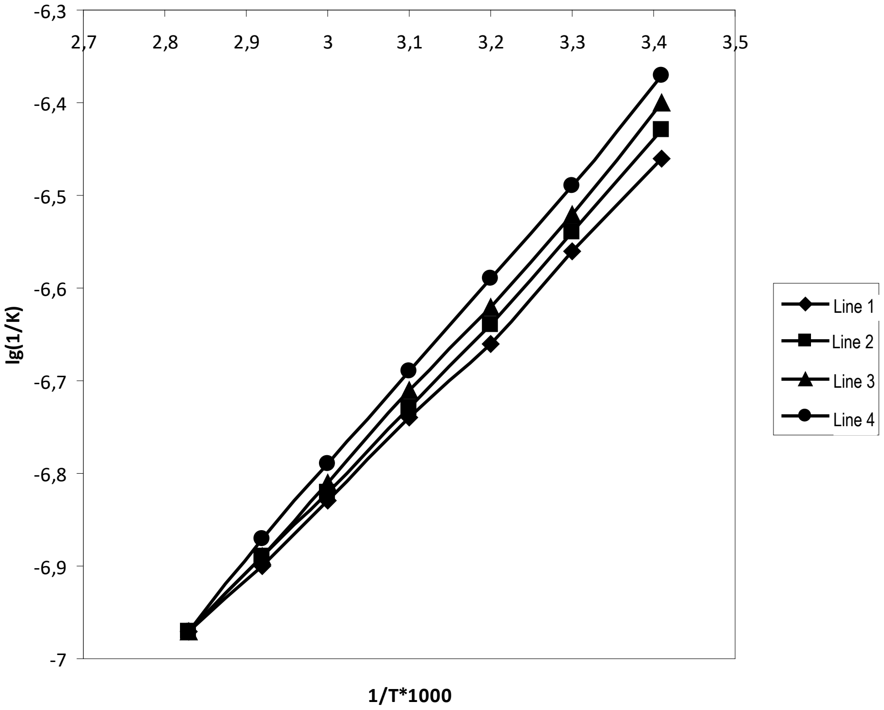

Fig. 1. Dependence of logarithm of inverse Henry's coefficients on inverse temperature for butadiene-1,3 solutions in potassium nitrate water-ammonia solutions with molar concentration of 0.1 mol/l at ammonia concentrations (mol/l) is: 1 - 0.0001; 2 - 0.001; 3 - 0.01; 4 - 0.1

An analysis of the aqueous solutions thermodynamic properties of non-electrolytes, which are weak proton acceptors, shows that the stabilization of the water structure decreases with heating. This results in negative enthalpy and entropy values. The negative enthalpy value reflects the hardening of the water structure during dissolution of the non-electrolyte. The ordering that occurs in this process appears in negative entropy values.

The thermodynamic functions of the dissolution processes were calculated from the experimental data on the solubility of butadiene-1,3 (Table 3).

Table 3. Thermodynamic functions of butadiene-1,3 dissolution processes in aqueous and aqueous-ammonia solutions at 25 ^{0}C

Composition of the solution	ΔH^0_{298}, kJ/mol	ΔG^0_{298}, kJ/mol	ΔS^0_{298}, J/(mol·K)
H_2O	-28.84	19.65	-164.22
KNO_3 (0,1 M)	-16.72	10.87	-91.54
KNO_3 (0,1 M), NH_3 (0,01 M)	-17.56	10.45	-94.05

A comparison of the thermodynamic functions numerical values of the hydrocarbon dissolution process [2] shows that both the enthalpy changes and the entropy change increase with increasing degree of unsaturation of the molecule. This is explained by the nature of the interaction between the solvent and the dissolved substance. The more heat is released during the formation of solutions, the higher its structural ordering should be, leading to a reduction in entropy. An increase of the dissolution heat of butadiene-1,3 in a aqueous-ammonia solution of potassium nitrate supports the assumption of hydrogen bonding between the hydrogen atoms of the ammonia molecule and the π-electrons of butadiene-1,3.

The decrease of Gibbs energy when the electrolyte is introduced into the solution determines the thermodynamic stability of the hydrocarbon solution. This value is greater for solutions of 2-methylpropene.

The thermodynamic characteristics of hydrated butadiene-1,3 (Table 4) in aqueous and aqueous-ammonia solutions were calculated using the equations:

$$L_{gas} + nH_2O \longleftrightarrow L_{aq}$$

$$(\Delta H^o_{298})^{\text{formation}} L_{aq} = (\Delta H^o_{298})^{\text{formation}} L_{gas} + (\Delta H^o_{298})_{\text{dissolving}},$$

$$(\Delta S^o_{298})^{\text{formation}} L_{aq} = (\Delta S^o_{298})^{\text{formation}} L_{gas} + (\Delta S^o_{298})_{\text{dissolving}},$$

$$(\Delta G^o_{298})^{\text{formation}} L_{aq} = (\Delta G^o_{298})^{\text{formation}} L_{gas} + (\Delta G^o_{298})_{\text{dissolving}}.$$

Table 4. Thermodynamic characteristics of hydrated butadiene-1,3 in aqueous and aqueous-ammonia solutions of KNO_3 (0.1 M) at 25 °C

Composition of the solution	ΔH^0_{298}, kJ/mol	ΔG^0_{298}, kJ/mol	ΔS^0_{298}, J/(mol·K)
H_2O	81.3	170.2	114.2
KNO_3 (0,1 M)	93.4	161.4	186.9
KNO_3 (0,1 M), NH_3 (0,01 M)	92.5	161.0	184.3

Conclusions

The influence of different degrees of unsaturated hydrocarbon on its solubility in aqueous-ammonia electrolyte solutions determined in this study can be further used to improve methods of hydrocarbons separation and purification.

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