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THERMODYNAMIC FUNCTIONS OF ACTIVATION FOR VISCOUS FLOW IN ELECTROLYTE-WATER-ORGANIC SOLVENT SYSTEMS

PART I. NaI SOLUTIONS IN MIXTURES OF WATER WITH ISOPROPANOL AND TERT-BUTANOL

Functions of activation for viscous flow ΔH^*, ΔS^*, and ΔG^* have been calculated for the systems NaI-water-isopropanol in the range of temperatures 288.15-313.15 K and NaI-water-tert-butanol in the range of temperatures 299.15-313.15 K. The calculations were made for NaI solutions with concentrations 0.5, 1.0 and 2.0 moles of salt per 100 moles of the solvent on the basis of our previous viscosity data. The results obtained have been interpreted from the point of view of alcohol effect on the water structure and that of NaI on a mixed solvent structure.

Introduction

In our earlier papers [1-3] we reported the results of viscosimetric investigations for the systems: NaI-water-isopropanol at 288.15, 298.15, 313.15 K and NaI-water-tert-butanol at 299.15, 308.15 and 313.15 K. Making use of these data and measured densities of NaI-water-tert-butanol system at 308.15 and 313.15 K, put in Table 2, the thermodynamic functions of activation of viscous flow have been calculated for both investigated systems.

Results and Discussion

As it is known the temperature dependence of liquid viscosity may be expressed by Eyring's equation [4]:

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Table 1

Mean molar volumes, V(cm^3mol^{-1}), of NaI solutions in water-isopropanol mixtures at 288.15, 298.15 and 313.15 K calculated on the base of density data from paper [1]; c - concentration of NaI in moles per 100 moles of mixed solvent

x_{IPA}%	c = 0			c = 0.5			c = 1.0			c = 2.0		
	288.15	298.15	313.15	288.15	298.15	313.15	288.15	298.15	313.15	288.15	298.15	313.15
0	18.03	20.08	18.16	18.11	18.15	18.25	18.20	18.25	18.35	18.36	18.42	18.54
1.5	18.82	18.86	18.95	18.90	18.94	19.05	18.98	19.03	18.52	19.14	19.21	19.33
5.0	20.58	20.65	20.80	20.70	20.73	20.89	20.73	20.82	20.98	20.90	20.99	21.16
7.5	21.82	21.95	22.15	21.91	22.03	22.23	22.00	22.11	22.32	22.16	22.28	22.50
10.0	23.14	23.29	23.54	23.22	23.37	23.62	23.30	23.45	23.71	23.47	23.62	23.87
15.0	25.87	26.07	26.41	25.95	26.14	26.48	26.03	26.22	26.55	26.18	26.37	26.64
20.0	28.70	28.95	29.34	28.76	29.00	29.39	28.83	29.07	29.43	28.94	29.16	29.56
25.0	31.57	31.83	32.29	31.61	31.87	32.32	31.66	31.92	32.37	31.75	32.00	32.44
30.0	34.45	34.77	35.27	34.47	34.79	35.28	34.51	34.83	35.31	34.57	34.88	35.35
40.0	40.26	40.67	41.27	40.25	40.67	41.26	40.26	40.64	41.24	40.25	40.66	41.24
50.0	46.11	46.62	47.36	46.08	46.57	47.30	46.04	46.51	47.26	45.98	46.45	47.16
60.0	52.04	52.60	53.46	51.96	52.52	53.36	51.91	52,46	53.28	51.79	52.28	53.12
70.0	57.99	58.65	59.60	57.89	58.52	59.46	57.78	58.42	59.35	57.60	58.21	59.13
80.0	63.99	64.71	65.78	63.84	64.57	65.60	63.71	64.41	65.44	63.45	64.12	65.13
85.0	67.00	67.75	68.88	66.82	67.57	68.66	66.66	67.38	68.48	66.36	67.07	68.13
90.0	69.98	70.83	72.08	69.79	70.60	71.74	69.61	70.38	71.62	69.29	70.05	71.22
92.5	71.53	72.33	73.56	71.33	72.10	73.30	71.12	71.88	73.13	70.72	71.45	72.62
95.0	73.07	73.87	75.14	72.85	73.62	74.86	72.65	73.39	74.63	72.27	73.01	74.18
97.5	74.61	75.42	76.71	74.39	75.16	76.43	74.15	74.93	76.20	73.74	74.47	75.71
100.0	75.19	76.91	78.25	75.92	76.07	77.99	75.64	76.39	77.72	75.17	75.90	77.21

$$\eta = \frac{hN}{V} \exp \frac{\Delta G^*}{RT} = \frac{hN}{V} \exp\left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R}\right) \tag{1}$$

where h is Planck's constant, V is molar volume of solution, N is Avogadro's number and ΔG^*, ΔH^* and ΔS^* are the free energy, enthalpy and entropy of activation, respectively. Equation (1) can be brought to (2) by including ΔS^* and V to constant A

$$\eta = A \cdot \exp \frac{\Delta H^*}{RT} \tag{2}$$

The form of equation (2) is essentially identical with Arrhenius' equation [4] so ΔH^* can be equated to E_{vis} (energy of activation) from Arrhenius' equation. Equation (2) lets us calculate mean enthalpy of activation of viscous flow (energy of activation), $\overline{\Delta H}^*$, from the function ln $\eta = f(1/T)$. The values of free energy of activation have been calculated by means of equation (1) in which V is a mean molar volume of the solution.

Table 1 shows the calculated values of mean molar volume of NaI solutions in mixtures of water with isopropanol (IPA) and in Table 2 there are values for NaI solution in the mixtures of water with tert-butanol (TBA) in all temperatures investigated. The calculated values ΔG^*, $\overline{\Delta H}^*$ and $T\Delta S^*$ for the mixtures of water with IPA and TBA and also for NaI solutions in these systems are presented in Tables 3-6.

Table 2

Densities, ρ (g.cm^{-3}), and mean molar volumes, V(cm^{3}mol^{-1}), of NaI solutions in water-tert-butanol mixtures at 299.15, 308.15 and 313.15 K c - NaI concentration in moles per 100 moles of the mixed solvent. Density data at 299.15 K are taken from paper [2]

x_a%	c = 0		c = 0.5		c = 1.0		c = 2.0	
	ρ_0	V	ρ	V	ρ	V	ρ	V
1	2	3	4	5	6	7	8	9
299.15 K								
0	0.99681	18.07	1.0279	18.16	1.0585	18.25	1.1172	18.44
5	0.9704	21.46	0.9962	21.55	1.0215	21.63	1.0702	21.82
10	0.9420	25.08	0.9645	25.15	0.9866	25.21	1.0283	25.38

Table 2 (contd)

1	2	3	4	5	6	7	8	9
20	0.8964	32.62	0.9139	32.65	0.9312	32.68	0.9654	32.74
30	0.8654	40.27	0.8799	40.26	0.8940	40.25	0.9223	40.23
40	0.8434	47.94	0.8553	47.94	0.8677	47.88	0.8911	47.81
50	0.8260	55.77	0.8367	55.68	0.8469	55.61	0.8675	55.45
60	0.8126	63.60	0.8222	63.45	0.8313	63.34	0.8496	63.10
70	0.8018	71.45	0.8104	71.26	0.8183	71.13	0.8347	70.81
80	0.7931	79.31	0.8007	79.10	0.8083	78.89	0.8235	78.46
90	0.7854	87.23	0.7930	86.91	0.8001	86.64	0.8184	85.67
95	0.7822	91.18	0.7892	90.86	0.7961	90.56	0.8100	89.95
100	0.7799	95.04	-	-	-	-	-	-
308.15								
0	0.99406	18.12	1.0249	18.22	1.0550	18.31	1.1135	18.50
5	0.9650	21.58	0.9910	21.66	1.0162	21.75	1.0647	21.93
10	0.9354	25.26	0.9566	25.36	0.9785	25.42	1.0202	25.59
20	0.8901	32.85	0.9055	32.95	0.9246	32.91	0.9558	33.06
30	0.8608	40.48	0.8748	40.49	0.8885	40.50	0.9162	40.50
40	0.8348	48.46	0.8469	48.42	0.8590	48.36	0.8819	48.31
50	0.8176	55.77	0.8283	56.24	0.8387	56.16	0.8587	56.02
60	0.8042	64.26	-	-	0.8227	64.00	0.8414	63.71
70	0.7930	72.25	0.8015	72.06	0.8099	71.87	0.8262	71.54
80	0.7842	80.21	0.7928	79.89	0.7995	79.75	0.8147	79.30
90	0.7765	88.23	0.7837	87.94	0.7909	87.65	0.8054	87.05
95	0.7732	92.24	0.7802	91.91	0.7872	91.59	0.8006	91.01
100	0.7711	96.13	0.7764	95.96	-	-	-	-
313.15								
0	0.99224	18.16	1.0230	18.25	1.0525	18.36	1.1110	18.54
5	0.9626	21.63	0.9883	21.72	1.0132	21.81	1.0623	21.98
10	0.9314	25.37	0.9531	25.45	0.9746	25.53	1.0168	25.67
20	0.8846	33.05	0.9017	33.09	0.9185	33.13	0.9522	33.19
30	0.8545	40.78	0.8686	40.78	0.8824	40.78	0.9100	40.77
40	0.8321	48.62	0.8438	48.59	0.8564	48.51	0.8792	48.46
50	0.8132	56.65	0.8234	56.58	0.8341	56.47	0.8544	56.30
60	0.7991	64.67	0.8087	64.51	0.8182	64.35	0.8366	64.08
70	0.7878	72.72	0.7965	72.51	0.8051	72.30	0.8214	71.96
80	0.7787	80.78	0.7865	80.53	0.7940	80.31	0.8096	79.80

Table 2 (contd)

1	2	3	4	5	6	7	8	9
90	0.7716	88.79	0.7785	88.53	0.7856	88.24	0.7996	87.68
95	0.7678	92.89	0.7743	92.61	0.7815	92.25	0.7954	91.60
100	0.7648	96.92	0.7716	96.55	-	-	-	-

Table 3

Functions of activation for viscous flow in water-isopropanol system; $\overline{\Delta H}^*$ - mean energy of activation in the range of temperatures: 288.15 - 313.15 K, ΔG^* - free energy of activation, ΔS^* - entropy of activation for viscous flow

x_a%	$\overline{\Delta H}^*$ kJmol^{-1}	ΔG^*, kJmol^{-1}			$T\Delta S^*$, kJmol^{-1}		
		288.15	298.15	313.15	288.15	298.15	313.15
0	16.79	9.44	9.43	8.83	7.35	7.36	7.96
1.5	19.49	10.19	9.82	9.42	9.30	9.67	10.07
5.0	24.46	11.65	11.17	10.60	12.81	13.30	13.86
10.0	29.19	12.93	12.34	11.59	16.26	16.84	17.60
15.0	30.15	13.59	12.99	12.24	16.56	17.17	17.91
20.0	29.38	13.93	13.35	12.69	15.45	16.03	16.69
25.0	29.24	14.19	13.62	13.00	15.05	15.62	16.24
30.0	28.63	14.36	13.82	13.23	14.28	14.82	15.41
40.0	27.25	14.54	14.06	13.54	12.71	13.18	13.70
50.0	26.04	14.62	14.20	13.74	11.42	11.84	12.30
60.0	24.97	14.66	14.28	13.87	10.30	10.69	11.09
70.0	23.98	14.70	14.36	13.99	9.28	9.62	9.98
80.0	23.17	14.76	14.45	14.12	8.42	8.72	9.05
85.0	22.84	14.80	14.51	14.19	8.04	8.32	8.65
90.0	22.82	14.86	14.59	14.27	7.96	8.23	8.55
92.5	22.65	14.91	14.64	14.33	7.74	8.01	8.32
95.0	22.58	14.96	14.70	14.38	7.62	7.89	8.20
97.5	22.74	15.55	14.76	14.45	7.19	7.98	8.29
100.0	22.58	15.06	14.85	14.51	7.52	7.73	8.07

Table 4

Functions of activation for viscous flow in water-tert-butanol system; $\overline{\Delta H^*}$ - mean energy of activation in the range of temperatures of 299.15 - 313.15 K, ΔG^* - free energy of activation, ΔS^* - entropy of activation for viscous flow

x_a, %	$\overline{\Delta H^*}$ kJmol^{-1}	ΔG^*, kJmol^{-1}			$T\Delta S^*$, kJmol^{-1}		
		299.15	308.15	313.15	299.15	308.15	313.15
0	15.85	9.13	8.93	8.83	6.72	6.92	7.02
5	24.24	11.68	11.33	11.10	12.56	12.91	13.14
10	27.99	13.07	12.63	12.40	14.92	15.36	15.59
20	29.84	14.52	14.07	13.84	15.31	15.77	16.00
30	30.60	15.25	14.80	14.55	15.35	15.79	16.05
40	31.01	15.71	15.29	15.01	15.30	15.71	16.00
50	31.50	16.02	15.59	15.32	15.49	15.91	16.18
60	31.81	16.24	15.81	15.54	15.58	16.00	16.28
70	31.94	16.41	15.99	15.71	15.53	15.95	16.23
80	32.65	16.59	16.14	15.86	16.06	16.51	16.78
90	33.96	16.79	16.31	16.03	17.17	17.65	17.93
95	35.43	16.93	16.40	16.10	18.50	19.03	19.32
100	37.32	17.11	16.54	16.19	20.21	20.77	21.13

Table 5

Functions of activation for viscous flow of NaI solutions in water-isopropanol mixtures; $\overline{\Delta H^*}$ - mean energy of activation in the range of temperatures of 288.15-313.15 K, ΔG^* - free energy of activation, ΔS^* - entropy of activation for viscous flow, c - NaI concentration in moles per 100 moles of mixed solvent

x_{IPA}%	$\overline{\Delta H^*}$ kJmol^{-1}	ΔG^*, kJmol^{-1}			$T\Delta S^*$, kJmol^{-1}		
		288.15	298.15	313.15	288.15	298.15	313.15
1	2	3	4	5	6	7	8
			c = 0.5				
0	16.82	9.48	9.19	8.88	7.33	7.62	7.93
1.5	18.94	10.18	9.83	9.46	8.75	9.10	9.48
5.0	23.85	11.60	11.14	10.59	12.25	12.70	13.26
10.0	27.54	12.81	12.30	11.60	14.73	15.24	15.95
15.0	29.01	13.52	12.96	12.26	15.49	16.05	16.75

Table 5 (contd)

1	2	3	4	5	6	7	8
20.0	28.63	13.89	13.34	12.71	14.75	15.30	15.92
25.0	28.40	14.17	13.63	13.04	14.23	14.77	15.36
30.0	27.81	14.35	13.84	13.28	13.46	13.97	14.53
40.0	26.62	14.56	14.11	13.61	12.06	12.51	13.01
50.0	25.78	14.68	14.27	13.82	11.10	11.51	11.96
60.0	24.79	14.74	14.37	13.97	10.05	10.42	10.83
70.0	23.86	14.80	14.47	14.11	9.06	9.39	9.75
80.0	23.28	14.89	14.59	14.26	8.39	8.69	9.03
85.0	22.92	14.94	14.67	14.34	7.97	8.25	8.58
90.0	22.86	15.02	14.76	14.42	7.84	8.10	8.44
92.5	22.85	15.08	14.81	14.49	7.77	8.04	8.36
95.0	22.82	15.13	14.87	14.55	7.68	7.94	8.27
97.5	22.85	15.20	14.93	14.62	7.65	7.92	8.23
100.0	23.18	15.28	15.01	14.67	7.90	8.17	8.50
c = 1.0							
0	16.36	9.50	9.22	8.94	6.87	7.15	7.43
1.5	18.56	10.18	9.87	9.41	8.38	8.70	9.15
5	23.09	11.55	11.13	10.60	11.54	11.96	12.49
10	27.00	12.77	12.26	11.61	14.23	14.73	15.39
15	28.04	13.46	12.93	12.28	14.58	15.11	15.76
20	27.57	13.84	13.33	12.74	13.73	14.24	14.83
25	27.76	14.15	13.63	13.07	13.61	14.13	14.69
30	27.21	14.34	13.85	13.32	12.87	13.36	13.89
40	26.19	14.58	14.14	13.67	11.62	12.05	12.52
50	25.44	14.72	14.32	13.88	10.73	11.12	11.56
60	24.55	14.80	14.44	14.05	9.75	10.11	10.50
70	23.66	14.87	14.56	14.20	8.79	9.10	9.46
80	23.24	14.99	14.69	14.36	8.25	8.55	8.87
85	22.91	15.05	14.78	14.45	7.86	8.14	8.46
90	22.98	15.60	14.88	14.55	7.39	8.11	8.44
92.5	22.91	16.20	14.93	14.62	7.71	7.98	8.29
95	23.04	16.27	15.00	14.68	7.77	8.04	8.36
97.5	23.23	15.34	15.07	14.74	7.89	8.16	8.49
100	23.21	15.41	15.16	14.80	7.80	8.05	8.40

Table 5 (contd)

1	2	3	4	5	6	7	8
c = 2.0							
0	15.50	9.52	9.29	9.03	5.98	6.21	6.47
1.5	17.72	10.19	9.90	9.58	7.53	7.82	8.14
5.0	22.13	11.51	11.11	10.64	10.62	11.02	11.49
10.0	25.09	12.65	12.22	11.63	12.44	12.87	13.46
15.0	26.35	13.37	12.90	12.31	12.98	13.45	14.04
20	26.41	13.79	13.31	12.78	12.62	13.10	13.63
25	26.62	14.12	13.64	13.13	12.50	12.98	13.49
30	26.36	14.34	13.89	13.39	12.02	12.47	12.97
40	25.63	14.61	14.21	13.75	11.02	11.42	11.88
50	25.03	14.80	14.41	14.00	10.23	10.62	11.03
60	24.32	14.92	14.56	14.19	9.41	9.76	10.13
70	23.43	15.01	14.70	14.37	8.42	8.73	9.06
80	23.13	15.16	14.87	14.56	7.97	8.26	8.57
85	22.87	15.24	14.98	14.66	7.63	7.90	8.21
90	22.84	15.35	15.10	14.78	7.49	7.74	8.06
92.5	23.01	15.42	15.16	14.84	7.59	7.85	8.17
95	23.12	15.49	15.23	14.91	7.63	7.89	8.21
97.5	23.92	15.57	15.31	14.98	7.74	8.01	8.33
100	23.23	15.64	15.40	15.05	7.59	7.82	8.18

Table 6

Functions of activation for viscous flow of NaI solutions in water-tert-butanol mixtures; $\overline{\Delta H^*}$ - mean energy of activation in the range of temperatures of 299.15-313.15 K, ΔG^* - free energy of activation, ΔS^* - entropy of activation for viscous flow, c - NaI concentration in moles per 100 moles of mixed solvent

x_{TBA}, %	$\overline{\Delta H^*}$ kJmol^{-1}	ΔG^*, kJmol^{-1}			$T\Delta S^*$, kJmol^{-1}		
		299.15	308.15	313.15	299.15	308.15	313.15
1	2	3	4	5	6	7	8
c = 0.5							
0	15.62	9.17	8.99	8.88	6.45	6.64	6.72
5	23.35	11.64	11.32	11.10	11.70	12.03	12.25
10	27.00	13.04	12.64	12.42	13.96	14.36	14.58

Table 6 (contd)

1	2	3	4	5	6	7	8
20	29.28	14.53	14.10	13.88	14.75	15.18	15.40
30	30.22	15.28	14.86	14.61	14.93	15.35	15.61
40	30.53	15.76	15.36	15.09	14.77	15.16	15.43
50	31.09	16.10	15.69	15.42	14.99	15.40	15.66
70	32.13	16.53	16.09	15.82	15.61	16.04	16.32
80	32.93	16.71	16.25	15.99	16.22	16.68	16.94
90	34.31	16.94	16.45	16.15	17.37	17.86	18.16
95	36.75	17.11	16.55	16.24	19.64	20.21	20.51
100	43.21	-	16.73	16.06	-	26.48	27.15
c = 1.0							
0	15.23	9.20	9.04	8.93	6.04	6.20	6.31
5	22.64	11.62	11.32	11.11	11.02	11.32	11.53
10	26.22	13.02	12.64	12.43	13.21	13.59	13.79
20	28.29	14.53	14.13	13.92	13.76	14.17	14.38
30	29.78	15.30	14.97	14.67	14.48	14.81	15.12
40	30.58	15.81	15.41	15.14	14.77	15.17	15.44
50	31.18	16.15	15.74	15.48	15.03	15.44	15.70
60	31.66	16.40	15.99	15.72	15.25	15.67	15.94
70	32.21	16.62	16.19	15.92	15.59	16.01	16.28
80	33.07	16.82	16.37	16.10	16.25	16.70	16.97
90	34.95	17.08	16.58	16.28	17.87	18.37	18.67
95	35.92	17.27	16.70	16.39	19.65	20.23	20.54
c = 2.0							
0	14.71	9.27	9.10	9.03	5.45	5.61	5.69
5	21.16	11.58	11.33	11.14	9.58	9.83	10.03
10	24.65	12.99	12.65	12.47	11.66	12.00	12.18
20	27.53	14.55	14.17	13.98	12.99	13.37	13.56
30	29.03	15.36	14.96	14.75	13.67	14.07	14.28
40	30.05	15.89	15.51	15.25	14.16	14.54	14.80
50	30.55	16.00	15.87	15.64	14.55	14.68	14.91
60	31.83	16.56	16.14	15.88	15.26	15.69	15.94
70	32.63	16.80	16.36	16.10	15.83	16.28	16.53
80	33.62	17.05	16.58	16.30	16.58	17.04	17.32
90	36.10	17.36	16.84	16.56	18.74	19.26	19.54
95	38.17	17.60	17.01	16.68	20.58	21.17	21.49

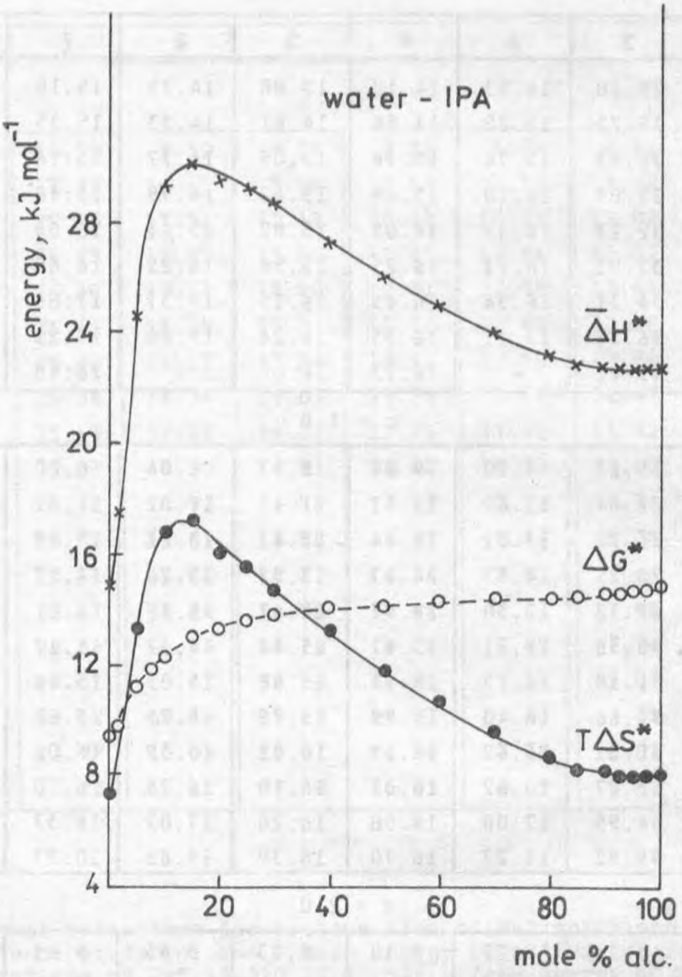

Fig. 1. Functions of activation of viscous flow in water-isopropanol mixtures at 298.15 K; ΔG^* - free energy, $\overline{\Delta H}^*$ - mean energy (in the range of temperatures of 288.15-313.15 K), ΔS^* - entropy of activation of viscous flow

In Figures 1 and 2 energy, entropy and free energy of activation of viscous flow are presented as a function of alcohol contents in mixtures of water with IPA and TBA. The energy and entropy of activation curves of both systems differ in their shapes. Both curves for water-IPA mixtures (Figure 1) go through the maxima

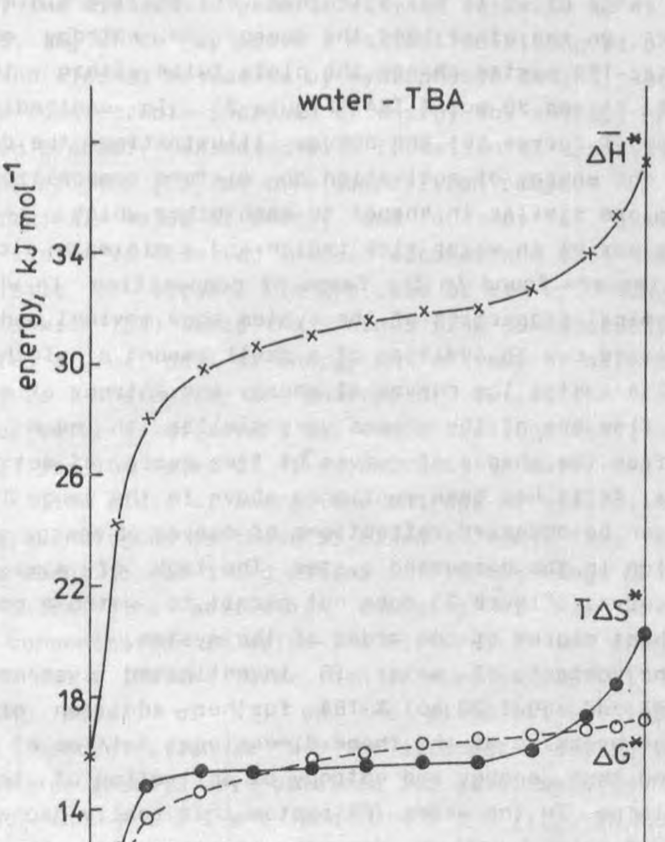

Fig. 2. Functions of activation of viscous flow in water-tert-butanol mixtures at 299.15 K; ΔG^* - free energy, $\overline{\Delta H^*}$ - mean energy (in the range of temperatures of 299.15-313.15 K), ΔS^* - entropy of activation of viscous flow

within the range of 10-15 mol % IPA and very shallow minima of about 95 mol % IPA. On the other hand the energy and entropy of activation in water-TBA system change the plots twice within the range 10-20 mol % TBA and 90 mol % TBA (Figure 2). In contradistinction to the shape of curves ΔG* the curves illustrating the dependence of entropy and energy of activation on mixture composition in water -IPA system are similar in shapes to each other which means that they show a maxima in water rich region and a minima in alcohol rich region. Maxima are found in the range of composition in which many physico-chemical properties of the system show maximal ordering of water structure due to addition of a small amount of alcohol [5-8]. In water-TBA system the curves of energy and entropy of activation of viscous flow are of the shapes very similar to each other and different from the shapes of curves of free energy of activation in this system. As it has been mentioned above in the range 10-20 mol % TBA there can be observed refractions of curves of energy and entropy of activation in the discussed system. The lack of maxima on ΔH* and TΔ S* curves (Figure 2) does not permit to watch a composition of the highest degree of the order of the system.

When the contents of water in investigated systems exceeds 15 mol % IPA and about 20 mol % TBA further addition of alcohol should cause breaking of the three-dimensional lattice of H - bonds in water and thus, energy and entropy of activation of viscous flow should diminish. In the water-IPA system this really happens so and the values of both functions decrease together with the increase of alcohol contents up to about 95 mol %, that is up to the composition being in accordance with the minimum of energy and etropy of activation. On the other hand in water-TBA system energy and entropy of activation grow to a very little degree together with the increase of alcohol content up to about 90% TBA. In the case of water-IPA system destroying water structure by IPA molecules and the process of creating various mixed associates probably dominante, hence a decreasing energy of activation can be observed. In water-TBA system the effect of destroying the water structure will be compensated by an association process, the latter leading to forming mixed associates of different structures. This will make the viscous flow difficult because of considerable branching of TBA molecules. About 90 mol % TBA and 95 mol % IPA the maximal number of associates of Brown and Ives-type [9] is probably formed. In water-TBA system the minimum of the dielectric permittivity is observed at ca. 90 mol % alcohol [9, 10] which may prove a maximal shielding of polar groups in water and alcohol molecules by hydrophobic chains. Above 90 mol % of TBA the considerable increase of energy and entropy of activation is observed probably connected with formation of a structure characteristic of alcohol [10] at this composition range.

The maximal value of energy and entropy of activation in water-TBA system is observed in pure alcohol and thus the structure characteristic of alcohol in the case of its branching molecules (as it is with TBA) makes the viscous flow considerably difficult and requires a great deal of energy and entropy of activation.

In figure 3 the energy and entropy of activation for viscous flow curves refer to different NaI concentrations (0.5, 1.0, 2.0 moles of salt per 100 moles of mixed solvent) in water-IPA mixtures at 298.15 K. The plots of energy and entropy of activation of NaI solution are analogous to these of mixed solvent. They go through the maxima about 15 mol % and minima within the range of composition 90-95 mol % IPA. The activation energies of NaI solution for different concentration in water-IPA mixtures in the range of composition 0-80 mol % IPA are lower than in pure solvent. It may suggest a destroying effect of NaI on the mixed solvent structure. The higher salt concentration we have the stronger destroying effect occurs. Similar results were obtained for water solution of NaI by Good [11] and Miller and Doran [12]. In NaI solutions containing more than 80 mol % IPA the activation energy exceeds the activation energy of the solvent, which may suggest that in this range of compositions NaI makes the ordering effect on the solvent structure.

While analysing the course of curves of activation entropies of NaI solutions and the solvent in this system in IPA rich regions it should be observed that above 90 mol % IPA the curves overlap in all temperatures investigated (Figure 3 and 4) on account of low values ΔS*. The activation entropies for the viscous flow of NaI solution containing from 0 to 90 mol % IPA are lower than in pure solvent so in this range of composition NaI destroys the structure of the mixture.

In Figure 5 can be found plots of activation energy and entropy of NaI solution (with salt concentration of 0.5, 1.0, 2.0 mole of electrolyte per 100 moles of solvent) in the mixtures of water with

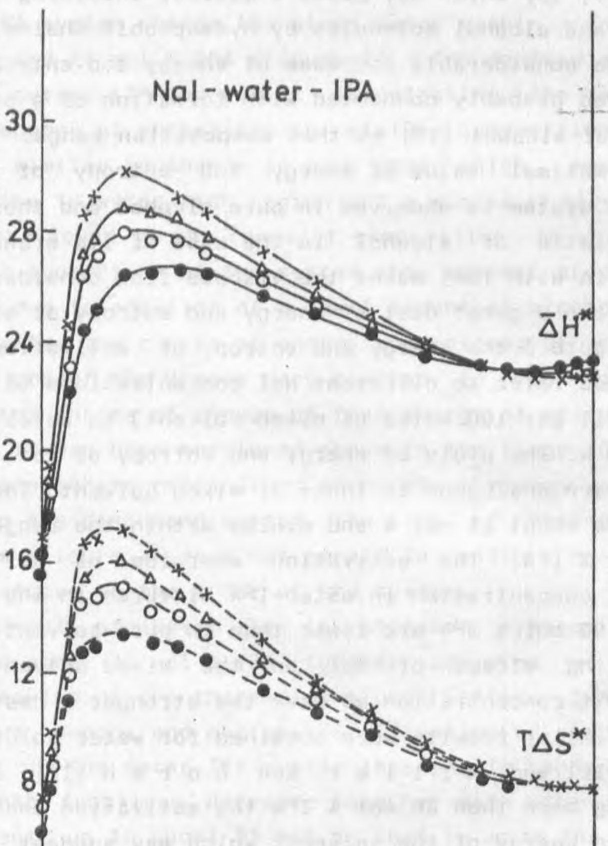

Fig. 3. Energy, ΔH^*, and entropy, $T\Delta S^*$, of activation of viscous flow of NaI solutions in water-isopropanol mixtures at 298.15 K; x - solvent, Δ - 0.5, o - 1.0, • - 2.0 moles of NaI per 100 moles of mixed solvent

TBA versus TBA content in the mixed solvent at 299.15 K. The shapes of the curves of activation energy and entropy of NaI solutions are analogous to the curve of the solvent. Together with the growth of TBA contents in the system both functions grow in the whole range

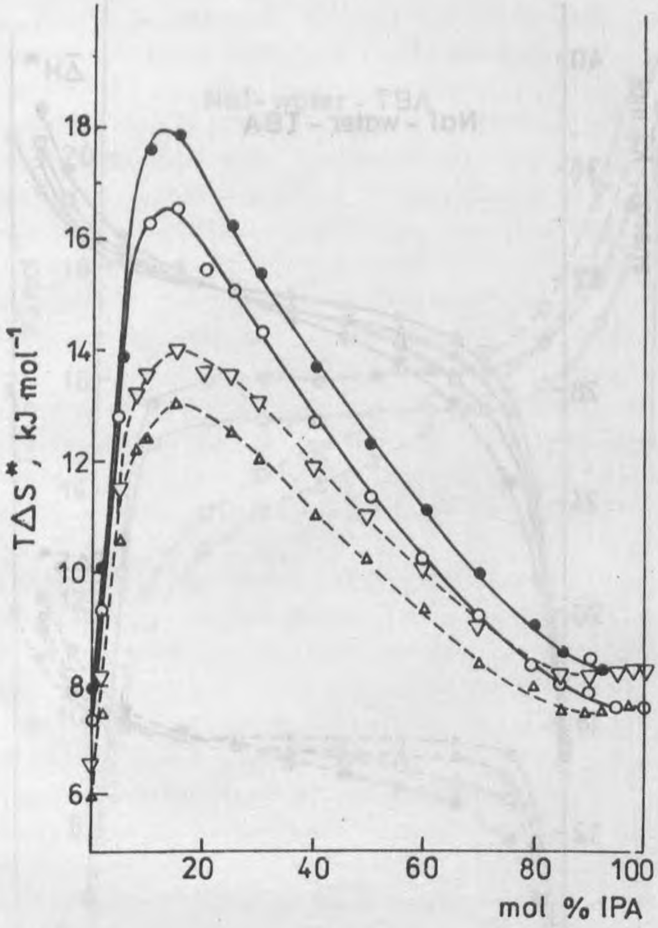

Fig. 4. Entropy of activation of viscous flow in water-isopropanol mixtures (full lines) and in NaI solutions in this mixture with concentration of 2.0 moles of salt per 100 moles of the mixed solvent (broken lines) at: o,▵ - 288.15 and •,▿ - 313.15 K

of composition of the solvent. At first, up to 20 mol % TBA the growth is rapid, then the curves change their courses and up to about 90 mol % TBA very little growth is observed. Above 90 mol % TBA again a fast growth of activation energy and entropy of both the solvent and NaI solutions can be seen. Energy and entropy of activation of NaI solutions are lower than the identical functions in pure solvent in the range of 0-65 mol % TBA, which, as it has

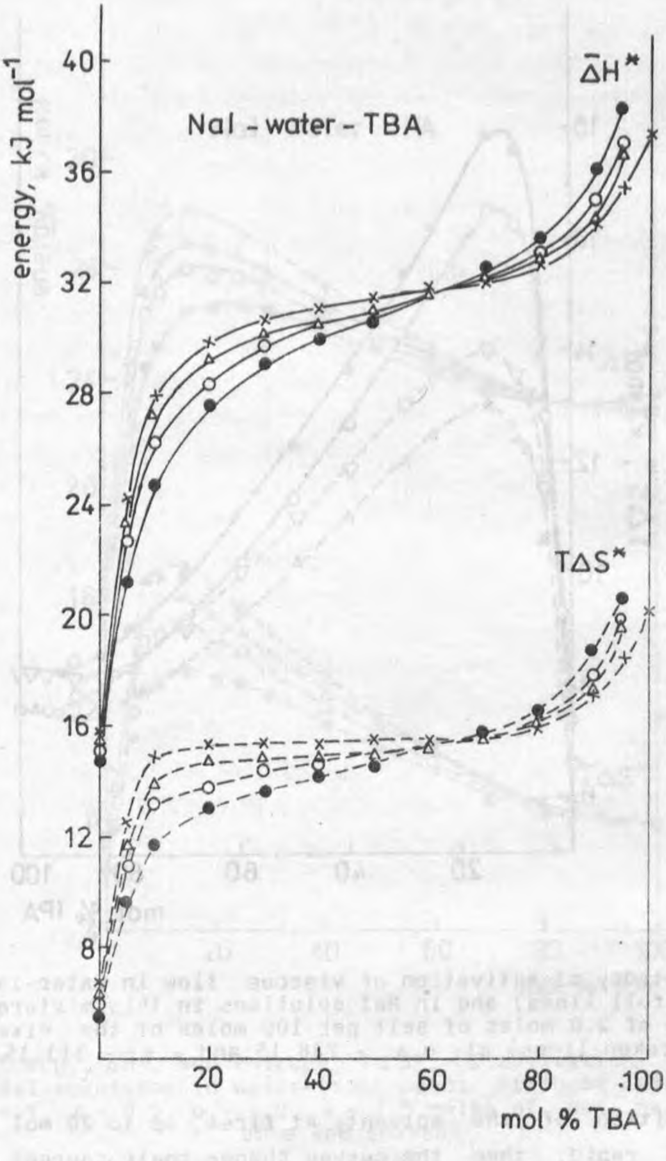

Fig. 5. Energy, $\overline{\Delta H}^*$, and entropy, $T\Delta S^*$, of activation for viscous flow of NaI solutions in water-tert-butanol mixtures at 299.15 K; × - solvent, Δ - 0.5, o - 1.0, • - 2.0 moles of NaI per 100 moles of solvent

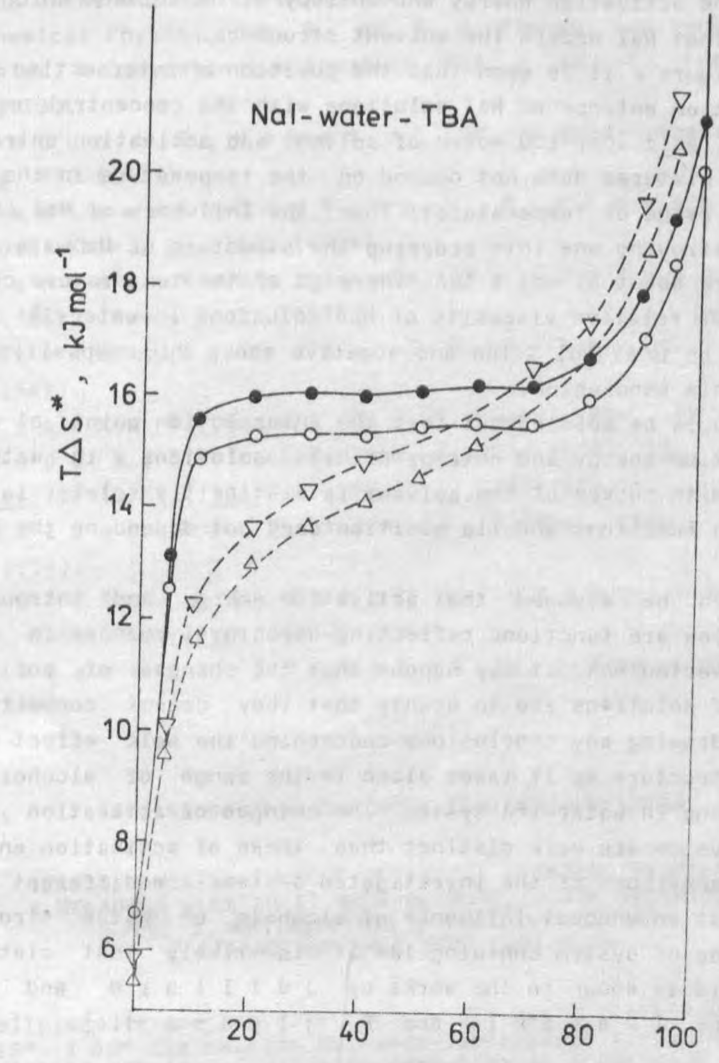

Fig. 6. Entropy of activation for viscous flow in water-tert-butanol mixtures (full lines) and of NaI solutions in this mixture with salt concentration 2.0 moles per 100 moles of the mixed solvent (broken lines) at: ○,△ - 308.15 K, ●,▽ - 313.15 K

been already mentioned before, suggest the destroying effect of the electrolyte on a mixed solvent structure. In NaI solutions with TBA contents higher than 65 mol % the activation energy and entropy exceeds the activation energy and entropy of the solvent which makes us think that NaI orders the solvent structure.

In Figure 6 it is seen that the position of intersection points of activation entropy of NaI solutions with the concentration of 2 moles of salt per 100 moles of solvent and activation entropy of water-TBA mixtures does not depend on the temperature in the investigated range of temperatures. Thus, the influence of NaI changes from a destroying one into ordering the structure of the water-alcohol mixture about 65 mol % TBA. The sign of the temperature coefficient of the relative viscosity of NaI solutions in water-TBA system (positive up to 65 mol % TBA and negative above this composition [3]) support this conclusion.

It should be pointed out that the intersection point of curves of activation energy and entropy of NaI solutions in water-TBA mixtures with curves of the solvent is distincltly clear in both activation functions and its position does not depend on the temperature.

It can be assumed that activation energy and entropy for viscous flow are functions reflecting structural changes in solutions. Nevertheless, it may happen that the changes of activation entropy of solutions are so scanty that they cannot constitute a base for drowing any conclusions concerning the salt effect on the solvent structure as it takes place in the range of alcohol rich compositions in water-IPA system. The changes of activation energy in this system are more distinct than these of activation entropy.

The behaviours of the investigated systems are different which may suggest an unequal influence of alcohols on water structure. In the case of system containg TBA it is likely that clathrates exist as it is shown in the works by Juillard and et al. [13] and by Iwasaki and Fujiyama [14].

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TERMODYNAMICZNE FUNKCJE AKTYWACJI LEPKIEGO PRZEPŁYWU W UKŁADACH ELEKTROLIT-WODA-ROZPUSZCZALNIK ORGANICZNY
CZĘŚĆ I. ROZTWORY NaI W MIESZANINACH WODY Z IZOPROPANOLEM I TERT-BUTANOLEM

Obliczono termodynamiczne funkcje aktywacji lepkiego przepływu ΔH^*, ΔS^* i ΔG^* dla układów NaI-woda-izopropanol w zakresie temperatur 288.15-313.15 K i NaI-woda-tert-butanol w zakresie temperatur 299.15-313.15 K. Obliczenia wykonano dla roztworów NaI o stężeniach 0.5, 1.0 i 2.0 mole soli na 100 moli rozpuszczalnika. Uzyskane wyniki zinterpretowano z punktu widzenia wpływu alkoholu na strukturę wody oraz NaI na strukturę mieszanego rozpuszczalnika.