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Stefania Taniewska-Osińska, Alina Piekarska

THERMODYNAMIC FUNCTIONS OF ACTIVATION OF VISCOUS FLOW IN NaI-WATER-AMIDE SYSTEMS

The thermodynamic parameters of viscous flow, namely: ΔH, ΔS at 298.15 K and ΔG in 278.15-318.15 K have been calculated for the systems NaI-water-formamide and NaI-water-N,N-dimethylformamide.

The calculations have been made on the basis of our previous viscosity data.

In our earlier papers [1] we reported the results of viscosimetric studies of NaI-water-formamide and NaI-water-DMF systems in the temperature range of 278.15-318.15 K. Taking advantage of those data we have now calculated the thermodynamic functions of activation of viscous flow in the two systems.

Results and discussion

As is well known, under constant pressure the temperature function of the viscosity of most liquids can be presented as an Arhenius equation

$$\eta = A_{exp} \frac{E_{vis}}{RT} \qquad (1)$$

where E_{vis} is molar activation energy of viscous flow, which can be determined as a slope of $\ln \eta$ relative to $1/T$. Another form of the dependence under discussion is the Eyring equation [2], which can be represented as:

$$\eta = \frac{hN}{V} \exp \frac{\Delta G^*}{RT} = \frac{hN}{V} \exp \left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \right) \qquad (2)$$

where h is Planck's constant, V is molal volume, N is Avogadro's number, and ΔG^*, ΔH^*, and ΔS^* are activation free energy, enthalpy and entropy respectively. Assuming that V and ΔS^* are constant, eqn 2 can be reduced to expression (3):

$$\eta = A\exp\frac{\Delta H^*}{RT} \qquad (3)$$

whose form is basically identical to that of eqn (1). In such a case ΔH^* can be compared to E_{vis}. Adopting the above assumption we have calculated ΔG^*, ΔH^* and ΔS^* for all NaI solutions in formamide and N,N-dimethylformamide with water in the temperature range of 278.15-318.15 K. The results are collected in Tab. 1-4.

Table 1

Formamide-water mixture activation parameters

Mol % F	ΔH_o^* kJ.mol^{-1}	ΔS_o^* e.u.	ΔG_o^*/kJ · mol^{-1}				
			278.15K	288.15K	298.15K	308.15K	318.15K
0	17.16	26.83	9.77	9.45	9.16	8.93	8.74
10	15.92	20.90	10.17	9.90	9.69	9.55	9.37
20	15.20	16.60	10.61	10.44	10.25	10.12	10.01
30	15.00	14.15	11.08	10.92	10.78	10.68	10.58
40	15.03	12.51	11.56	11.43	11.30	11.21	11.13
50	15.44	12.11	12.15	11.94	11.83	11.74	11.65
60	16.07	12.51	12.60	12.45	12.34	12.25	12.16
70	16.67	12.84	13.08	12.97	12.84	12.76	12.66
80	17.23	12.98	13.63	13.46	13.36	13.29	13.15
90	18.27	14.69	14.16	14.03	13.89	13.81	13.63
100	19.86	18.28	14.77	14.56	14.41	14.26	14.10

Table 2

Activation parameters of NaI-water-formamide system

NaI[a]	Mol % F	ΔH* kJ.mol^{-1}	ΔS* e.u.	ΔG*/kJ · mol^{-1}				
				278.15K	288.15K	298.15K	308.15K	318.15K
0.5	0	16.77	25.46	9.76	9.45	9.18	8.97	8.78
	10	15.73	20.09	10.19	9.95	9.74	9.60	9.43
	20	15.10	16.03	10.66	10.50	10.32	10.18	10.01
	30	15.02	13.95	11.15	11.01	10.86	10.72	10.60
	40	15.13	12.51	11.66	11.52	11.40	11.31	11.23
	50	15.62	12.38	12.19	12.06	11.93	11.85	11.76
	60	16.42	12.81	12.72	12.58	12.46	12.38	12.27
	70	17.02	12.98	13.24	13.10	12.97	12.87	12.78
	80	17.60	14.29	13.77	13.60	13.48	13.37	13.27
	90	18.68	15.63	14.24	14.17	14.03	13.93	13.75
	100	20.26	19.15	14.86	14.71	14.53	14.38	14.22
1	0	16.40	24.18	9.76	9.45	9.19	8.99	8.83
	10	15.40	18.95	10.21	9.99	9.79	9.67	9.50
	20	14.95	15.46	10.73	10.56	10.39	10.26	10.10
	30	14.95	13.38	11.25	11.10	10.96	10.86	10.75
	40	15.27	12.61	11.78	11.64	11.51	11.41	11.32
	50	15.87	12.31	12.33	12.19	12.07	11.98	11.86
	60	16.64	12.71	12.89	12.73	12.61	12.52	12.35
	70	17.27	13.62	13.41	13.27	13.14	13.03	12.75
	80	17.90	15.09	13.91	13.75	13.60	13.49	13.34
	90	18.94	16.64	14.48	14.37	14.15	14.02	13.89
	100	20.54	20.33	15.06	14.86	14.66	14.49	14.33
2	0	15.78	21.99	9.76	9.49	9.22	9.07	8.92
	10	15.20	17.84	10.29	10.06	9.88	9.77	9.62
	20	14.93	14.76	10.85	10.69	10.53	10.42	10.32
	30	15.10	13.38	11.40	11.25	11.11	11.00	10.91
	40	15.50	12.78	11.97	11.83	11.69	11.55	11.50
	50	16.18	13.11	12.55	12.41	12.27	12.18	12.09
	60	17.06	13.79	13.13	12.98	12.85	12.74	12.65
	70	17.77	14.69	13.69	13.54	13.39	13.28	13.18
	80	18.51	16.03	14.20	14.05	13.88	13.76	13.63
	90	19.57	17.54	14.77	14.61	14.41	14.30	14.16
	100	21.30	21.23	15.40	15.17	14.97	14.79	14.62

[a] NaI conc. in moles of NaI in 100 mol mixed solvent.

Table 3

N,N-dimethylformamide-water mixture
activation parameters

Mol % DMF	ΔH_o^* kJ.mol^{-1}	ΔS_o^* e.u.	ΔG_o^*/kJ · mol^{-1}				
			278.15K	288.15K	298.15K	308.15K	318.15K
0	17.16	26.83	9.77	9.45	9.16	8.93	8.74
5	19.58	30.42	11.16	10.80	10.51	10.24	9.98
10	21.67	34.17	12.22	11.85	11.48	11.19	10.93
15	23.08	36.39	13.01	12.63	12.26	11.95	11.64
20	23.63	36.42	13.50	13.15	12.77	12.46	12.14
25	23.81	35.85	13.85	13.47	13.12	12.83	12.50
30	23.35	33.60	14.01	13.67	13.34	13.06	12.75
35	22.37	29.92	14.02	13.74	13.45	13.18	12.92
40	21.00	25.29	13.97	13.64	13.46	13.25	13.02
50	18.14	16.10	13.70	13.44	13.34	13.21	13.13
60	15.57	8.18	13.32	13.19	13.13	13.07	13.09
70	13.51	1.98	12.96	12.91	12.92	12.92	12.95
80	11.65	-3.59	12.65	12.67	12.72	12.78	12.87
90	10.17	-8.12	12.41	12.51	12.59	12.68	12.80
100	9.11	-11.30	12.29	12.36	12.48	12.67	12.84

Table 4

Activation parameters of NaI-water-N,N-dimethylformamide system

NaI[a]	Mol % DMF	ΔH* kJ.mol^{-1}	ΔS* e.u.	ΔG* kJ . mol^{-1}				
				278.15K	288.15K	298.15K	308.15K	318.15K
	0	16.77	25.46	9.76	9.45	9.18	8.97	8.78
	5	19.25	29.25	11,16	10.82	10.53	10.27	10.03
	10	21.40	33.17	12.23	11.87	11.51	11.27	10.98
	15	22.83	35.32	13.03	12.65	12.30	12.00	11.70
	20	23.40	35.52	13.52	13.19	12.81	12.52	12.20
	25	23.59	34.92	13.90	13.52	13.18	12.90	12.58
	30	23.33	33.27	14.08	13.74	13.41	13.15	12.84
0.5	35	22.46	29.88	14.11	13.83	13.55	13.27	13.01
	40	21.23	25.69	14.09	13.75	13.57	13.36	13.12
	50	18.46	16.77	13.84	13.57	13.46	13.34	13.24
	60	15.90	9.35	13.31	13.07	13.11	13.05	13.20
	70	13.85	2.68	13.11	13.05	13.05	13.05	13.08
	80	12.03	-2.78	12.80	12.82	12.86	12.94	13.00
	90	10.53	-7.35	12.55	12.65	12.72	12.85	12.92
	100	9.48	-10.50	12.44	12.50	12.61	12.78	12.95
	0	16.40	24.18	9.76	9.45	9.19	8.99	8.83
	5	18.95	28.20	11.16	10.83	10.54	10.30	10.08
	10	21.13	32.27	12.20	11.88	11.53	11.27	11.03
	15	22.68	34.71	13.07	12.65	12.33	12.04	11.75
	20	23.35	35.18	13.60	13.20	12.86	12.57	12.25
	25	23.58	34.68	13.95	13.57	13.24	12.95	12.63
	30	23.33	33.04	14.17	13.79	13.48	13.22	12.92
1	35	22.68	30.35	14.23	13.89	13.63	13.35	13.09
	40	21.40	25.96	14.18	13.85	13.66	13.44	13.29
	50	18.67	17.07	13.96	13.70	13.58	13.44	13.36
	60	16.23	9.49	13.61	13.47	13.40	13.33	13.32
	70	14.20	3.38	13.26	13.20	13.19	13.19	13.20
	80	12.32	-2.28	12.95	12.96	13.00	13.05	13.11
	90	10.83	-6.84	12.71	12.80	12.87	12.94	13.05
	100	9.77	-10.00	-	12.66	12.75	12.94	13.09

Table 4 cont.

NaI[a]	Mol % DMF	ΔH* kJ.mol^{-1}	ΔS* e.u.	ΔG* kJ · mol^{-1}				
				278.15K	288.15K	298.15K	308.15K	318.15K
	0	15.78	21.99	9.76	9.49	9.22	9.07	8.92
	5	18.32	25.89	11.17	10.86	10.60	10.37	10.17
	10	20.62	30.25	12.27	11.92	11.60	11.35	11.14
	15	22.23	32.97	13.10	12.75	12.40	12.13	11.87
	20	23.08	33.67	13.64	13.32	12.96	12.68	12.40
	25	23.37	33.54	14.06	13.70	13.37	13.09	12.80
	30	23.12	31.83	14.29	13.93	13.63	13.36	13.11
2	35	22.79	30.15	14.38	14.10	13.80	13.53	13.27
	40	21.75	26.46	14.41	14.05	13.86	13.64	13.41
	50	19.18	17.94	14.23	13.95	13.83	13.64	13.59
	60	16.72	10.23	13.89	13.75	13.67	13.59	13.58
	70	14.70	4.09	13.56	13.49	13.48	13.46	13.47
	80	12.79	-1.68	13.26	13.26	13.29	13.33	13.40
	90	11.29	-6.27	13.02	13.10	13.16	13.24	13.34
	100	10.23	-19.39	-	12.95	13.03	13.22	13.38

[a] NaI conc in moles of NaI in 100 mol mixed solvent.

Activation enthalpy of viscous flow (ΔH*) of water-formamide mixtures and of NaI solutions in these mixtures Fig. 1 decreases in the range of 0% mole to 15-20% mole formamide, which is probably due to the destructive effect of formamide on water structure: the formation of small and homogeneous or mixed aggregates facilitates viscous flow. The minimum point (15-20% mole F) probably corresponds to total destruction of the three-dimensional H-bond lattice in water. The formation of larger mixed formamide-water associates produces an increase in the activation enthalpy of viscous flow in the range of ~20%- ~90% mole formamide. In the 90-100% mole range a much faster increase in ΔH* is observed both in NaI solutions in water-formamide mixtures and in the mixed solvent. Quite likely, solutions containing more than 90% mole formamide develop a formamide

structure typical of pure liquid which, in turn, makes viscous flow more difficult and requires more energy. The activation energy of viscous flow in NaI solutions in water-formamide mixtures in the range of 0-25% mole F is lower than that for pure solvent. This may be related to the structure breaking effect of the ions introduced on the mixed solvent. The opposite course of the two functions in the range of formamide contents exceeding ~25% mole suggests that NaI has an ordering effect on the solvent structure.

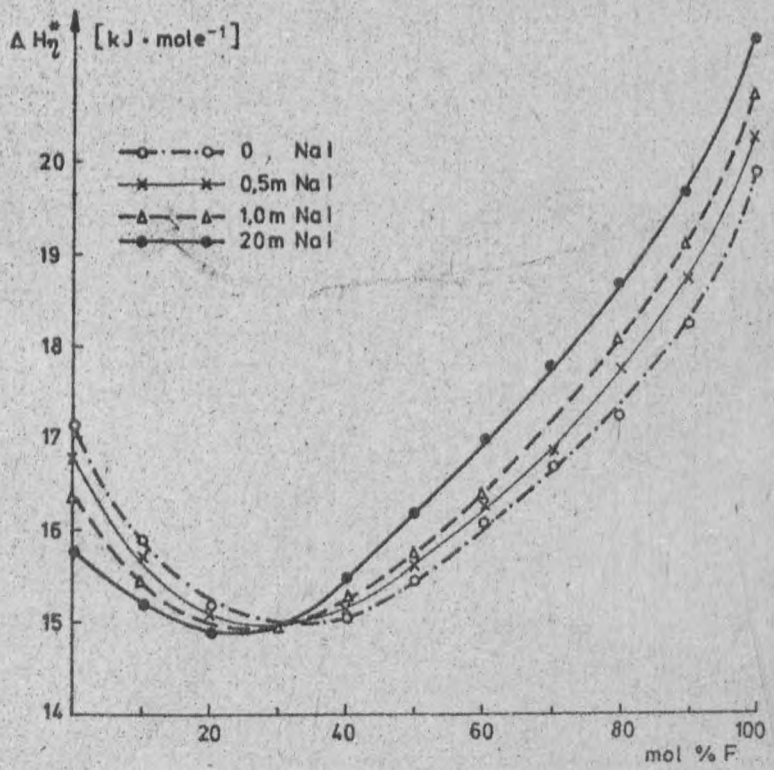

Fig. 1. Activation energy for viscous flow of NaI solutions in water-formamide mixtures at 298.15K. Electrolyte concentration in mole NaI per 100 mole of mixed solvent

A different course of the $\Delta H^* = f$ (% mole amide) function is observed both in the case of DMF mixture with water and in the case of NaI solutions in such mixtures (Fig. 2). The activation enthalpy of viscous flow in this system exhibits maxi-

mum in the area corresponding to maximum viscosity of these systems. The above finding seems to confirm the idea - put forth earlier [1] - that in the range of contents under discussion the H-bonds have maximum density. Similarly as in the case of the previously discussed system, the activation enthalpy of viscous flow of NaI solutions in the range of 0-25% mole DMF is lower than the activation energy of pure solvent. This is probably due to the destructive effect of the ions introduced on the solvent aggregates. In solutions containing more than 25% mole DMF, ΔH^* of the solution is higher than ΔH^* of the solvent,

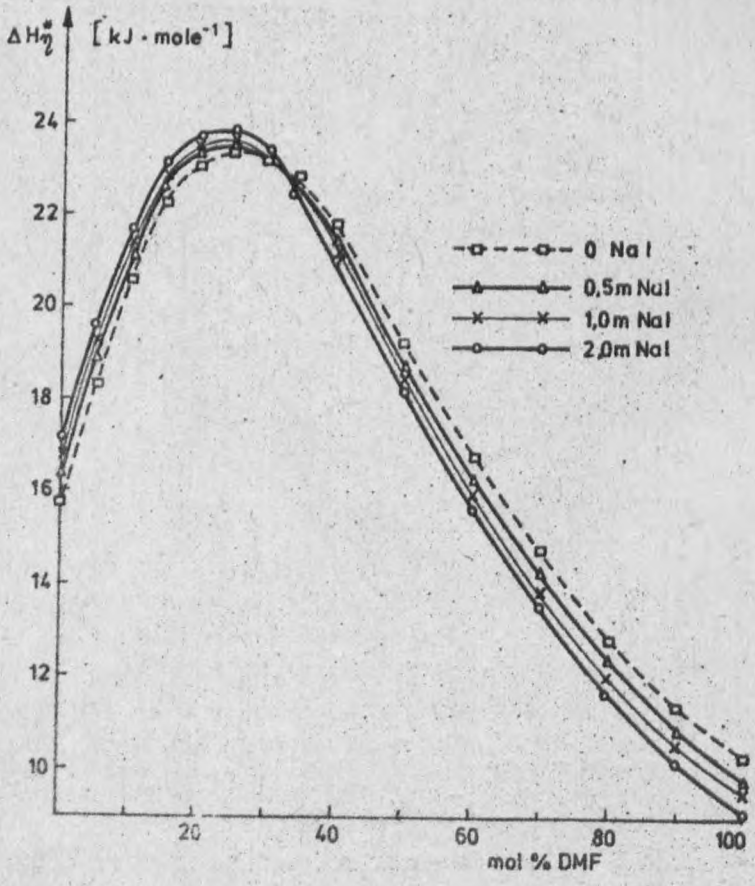

Fig. 2. Activation energy for viscous flow of NaI solutions in water-DMF mixtures at 298.15 K. Electrolyte concentration in mole NaI per 100 mole of mixed solvent

possibly due to the ordering effect of NaI on the structure of the DMF-water mixture.

A different shape of the $\Delta H^* = f$ (% mole amide) function in DMF-water system in comparison to that in formamide-water system, as can be seen in Figs. 1 and 2 is probably due to the hydrophobic hydration which can undergo two methyl groups in DMF molecule.

References

[1] S. Taniewska-Osińska, A. Piekarska, A. Kacperska, J. Solution Chem. 12 (10), 717 (1983).

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Department of Physical Chemistry
University of Łódź

Stefania Taniewska-Osińska, Alina Piekarska

FUNKCJE TERMODYNAMICZNE AKTYWACJI LEPKIEGO PRZEPŁYWU W UKŁADACH NaI-WODA-AMID

Obliczono termodynamiczne funkcje aktywacji lepkiego przepływu ΔH^*, ΔS^* w temperaturze 298.15 K oraz ΔG^* w zakresie temperatur 278.15-318.15 K dla układów NaI-woda-formamid oraz NaI-woda-N,N-dwumetyloformamid. Obliczenia wykonano na podstawie wcześniejszych danych lepkości. Entalpia aktywacji lepkiego przepływu, w zależności od zawartości amidu, w układzie NaI-woda-formamid przechodzi przez minimum w obszarze zawartości formamidu 15-20% mol. Przebieg analogicznej zależności w układzie NaI-woda-DMF wykazuje maksimum w przedziale 25-30% mol DMF.

Стефания Таневска-Осиньска, Алина Пекарска

ТЕРМОДИНАМИЧЕСКИЕ ФУНКЦИИ АКТИВАЦИИ ВЯЗКОГО ТЕЧЕНИЯ В СИСТЕМАХ NaI-ВОДА-АМИД

На основе опубликованых раньше данных о вязкости вычислены термодинамические функции активации вязкого течения ΔH^* и ΔS^* при температуре 298.15 К и ΔG^* в диапазоне температур 278.15–318.15 К для систем NaI-вода-формамид и NaI-вода-ДМФ. Энтальпия активации ΔH^* как функция состава растворителя в системе NaI-вода-формамид проходит через минимум отвечающий 15–20 мол % формамида.

Аналогическая функция для системы NaI-вода-ДМФ проходит через максимум в растворах содержащих 25–30 мол % ДМФ.