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Transport and thermodynamic properties of sodium carboxymethylcellulose in dimethyl sulfoxide - water mixed solvent media at 298.15, 303.15, 308.15, and 313.15 K

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Research Article

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Transport and thermodynamic properties of sodium carboxymethylcellulose in dimethyl sulfoxide - water mixed solvent media at 298.15, 303.15, 308.15, and 313.15 K

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ABSTRACT:

Equivalent conductivity values of solutions of sodium carboxymethylcellulose in dimethyl sulfoxide-water mixed solvent have been evaluated at varying sodium carboxymethylcellulose concentration, solvent composition and temperature. These experimental data corresponding to the semi dilute regime have been analysed on the basis of the dynamic scaling model for polyion chains proposed by Dobrynin et al. The analysis reveals that with the increase in the value of square root of the polyelectrolyte concentration, the fraction of free counterions decreases suggesting that counterion condensation is favoured at higher polyelectrolyte concentration. It was observed that polyions were responsible for transporting the bulk of the current and the polyions were also found to experience increased frictional resistance in solution with increased dimethyl sulfoxide content in the mixed solvent as well as with the decrease in temperature. These results and observations were qualitatively in line with similar studies carried out with different solvent systems but were quantitatively different.

Keywords: Sodium carboxymethylcellulose, Dimethyl sulfoxide-water mixed solvent, Polyion-counterion interactions, Electrical conductivity, Counterion condensation, Thermodynamics

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Introduction

Polymers containing ionizable groups in their monomer units which when dissolved in polar solvents dissociate to form polyions and counterions are known as polyelectrolytes. These polyion chains are extended due to electrostatic repulsion between the like charges on the polyion backbone [1, 2]. Counterion condensation on the polyion chain screens these electrostatic interactions leading to coiling and contraction of the polyion chains. Factors affecting these interactions between the polyions and counterions like relative permittivity of the solvent, temperature, polyelectrolyte concentration etc has a profound effect on the transport and thermodynamic properties of the solutions of the polyelectrolytes [3]. Certain properties of polyelectrolytes like their solubility in water, ionic conductivity, inter and intra chain interactions, surface activity and their biocompatibility especially the natural polyelectrolytes make them exciting candidates for drug delivery applications [4]. Natural polyelectrolytes or bio-polyelectrolytes like proteins or polysaccharides are fundamentally important and an understanding of their behavior in physiological settings would be immensely valuable to manipulate them for the development of healthcare materials [5, 6]. The solution properties including the transport properties of the polyelectrolytes can be readily investigated with the help of conductance studies as these depend on the movement of polyions and counterions caused by an applied electric field [7].

There is no dearth of literature based on the conductivity studies of various types of polyelectrolytes like natural, synthetic or chemically modified natural polyelectrolytes [8-10]. However, there are a limited number of studies which delves into the effect of dielectric constant or temperature on the thermodynamic as well as the transport properties of polyelectrolytes [11-13]. The present study is a continuation of our past efforts to elucidate polyion- counterion interactions under the influence of changing temperature and relative permittivity which can be achieved by changing the composition of the binary solvent used. The current study reports the conductance studies of sodium carboxymethylcellulose (NaCMC) solutions of varying concentration in dimethyl sulfoxide (DMSO) – water mixed solvent systems of varying compositions at four different temperatures. The data has been analysed using the model proposed by Colby et al (1997) [14] which in turn is based on the scaling theory of polyelectrolytes as proposed by Dobrynin et al. [15]. The effects of temperature and varying NaCMC and DMSO content in ternary solutions of NaCMC, DMSO and water on some selected transport and thermodynamic parameters like the fraction of uncondensed counterions, equivalent conductivities

and transference numbers of polyion, the solvodynamic friction coefficients of the polyion in solution and the free energies of counter ion association have been studied in order to derive a better understanding of the counterion - polyion interactions and their consequences.

Theory

The experimentally obtained equivalent conductance data obtained in this study has been analysed using Colby's model [14] which utilises the scaling description of polyelectrolytes [15] for the electrical conductivity of salt-free semi dilute polyelectrolyte solutions. Under these conditions, the polymer chain behaves as a random walk of N_ξ correlation blobs with each 'unit' containing g monomers and having a size of ξ_0. The charge carried by each blob denoted by $q_\xi = z_c efg$ (where z_c is the counter ion valency, e is the charge of an electron, and f is the fraction of uncondensed counterions). The maximum end to end length of the polyion chain (contour length) is given by $L = N_\xi \xi_0$, and the charge carried by the chain is $Q_p = N_\xi q_\xi = z_c efg\, N_\xi$. When the length scales is less than ξ_0 the polymer chain containing g_e electrostatic blobs of size ξ_e takes on a fully extended conformation because the electrostatic interactions dominate in this scenario. However, if the length scales is greater than ξ_0, the chain is a random walk of correlation blobs of size ξ_0 because the hydrodynamic interactions are screened.

In semi dilute solution without any added salt the equivalent conductivity of the polyion as per this model is given by

$$\lambda_p = \frac{F z_c efc \xi_0^2}{3\pi\eta_0} \ln\left(\frac{\xi_0}{\xi_e}\right) \qquad (1)$$

where the Faraday constant is denoted by F, c is the number of groups carrying unit charge per ml, the coefficient of viscosity is given by η_0 and the significance of the other remaining symbols have been described in the preceding paragraph.

On the other hand, for the polyelectrolyte solution, the equivalent conductivity is given by the following equation (Colby et al., 1997) [14]

$$\Lambda = f\left[\lambda_c^0 + \frac{Fz_c efc\xi_0^2}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_e}\right)\right] \qquad (2)$$

where λ_c^0 is the equivalent conductivity of the counter ion at infinite dilution.

Colby [14] has considered *f* to be a variable parameter and with the help of this new approach this adjustable parameter can be easily determined experimentally. Literature survey reveals that this model has been successfully applied to a handful of aqueous polyelectrolytes [16, 17]. This model has also been applied to a few polyelectrolytes in mixed solved media [11, 18, 19]. Even amongst these few systems studied, the limited solubility of the polyelectrolytes in some of the mixed solvent systems restricted these studies to a narrow solvent composition. The common feature of all these studies is the good agreement of the calculated values with those obtained experimentally which is very commendable. Based on the values of *f* observed, this model has also been used to identify whether the polyelectrolyte solution under investigation belongs to the dilute, semi-dilute or concentrated concentration regimes [17, 19]. In the present study, DMSO has been chosen as the solvent to be mixed with water because it has a relatively high dielectric constant and hence, can stabilize charged species in solution. Furthermore, when DMSO is mixed with water, it tends to be caged in by water molecules [20] and still retain its rotational freedom. The DMSO-water complex is stabilized by one primary OH… OS hydrogen bond and two weaker CH…OH, hydrogen bonds [21]. A study of the behaviour of the polyelectrolyte NaCMC in such an interesting mixed solvent media may yield exciting results.

Materials and methods

Materials

Analytical grade DMSO procured from E. Merck, India. The molecular sieves used was heated to 200°C to remove adsorbates like moisture and subsequently used to dry DMSO which was then vacuum distilled over sodium carbonate to minimize its decomposition during distillation. The water used for preparing solvents were subjected to three cycles of distillation and its specific conductance was found to be negligible ($<10^{-6}$ S cm^{-1}) at room temperature. The physical properties, namely density, viscosity, and dielectric constant of the mixed solvent containing 10, 20, 30 and 40 % of DMSO by mass at temperatures 298.15, 303.15, 308.15, and 313.15 K are given in Table 1. The equivalent conductivities of the sodium counterion (Na^+) at infinite dilution, λ_c^0 in (DMSO + water) mixtures containing 10, 20, 30 and 40% of DMSO by mass are taken from our previous study [22] and are also included in Table 1. Literature values of these physical properties where available are also shown for comparison purposes [23]. It can be observed that there are no significant differences between the experimental values obtained in this study and the available literature values.

Sodium carboxymethyl cellulose (NaCMC) utilized in the current investigation was obtained from Sigma-Aldrich. Its mass average molar mass was 90,000 and its degree of substitution was 0.7. These two characteristics of NaCMC were evaluated as reported earlier by (Sharma et al 2010) [24] and agreed well with those claimed by the manufacturer. The solutions were meticulously prepared in a dehumidified chamber to prevent moisture absorption.

Conductivity measurements

An Orion 3-Star conductivity meter consisting of a dip type cell (cell constant = 1.14 cm^{-1}, uncertainty = 0.01%) working at 2000 Hz was used to measure the specific conductance of the ternary solutions comprising of the polyelectrolyte (NaCMC), DMSO and water at four different temperatures, viz, 298.15, 303.15, 308.15 and 313.15 K. The specific conductances of DMSO-water mixed solvents at each experimental temperature were also measured and these values were subtracted from the corresponding specific conductance values of NaCMC solutions. A temperature-controlled water bath (with an uncertainty of ±0.05°K) was used to measure the

conductance of the ternary solutions at the above-mentioned temperatures. The experimental procedure followed as well as the set-up used was similar to that reported by Das & Hazra [25]. The precision of the results was ensured by repeating each experiment thrice, and the average of the results were taken. Experimentally the equivalent conductivities (Λ) of solutions of NaCMC in DMSO-water mixture were evaluated at various polyelectrolyte concentrations and temperatures.

Viscosity measurements

The viscosity of mixed solvents was measured using a suspended level viscometer. The flow time of distilled water at 25 °C was observed to be about 539 s. The detailed experimental procedure has been described earlier [29].

Results and discussion

Variation of equivalent conductivities with polyelectrolyte concentration

Fig. 1a-1d. depicts the changes in equivalent conductance (Λ) with respect to $\sqrt{c_p}$ (where c_p is the concentration of the polyelectrolyte solution in equivalents per litre units) in solvent systems containing 10%, 20%, 30%, and 40% DMSO by mass respectively at four different temperatures. From the figure it is clear that at a given solvent composition Λ increases markedly with increase in temperature within the range of c_p employed. A slight decrease in Λ values with increase in polyelectrolyte concentration is observed at constant solvent composition and temperature. The calculated values of Λ using Colby's model agrees very well with the experimentally obtained values of Λ, considering the solvent system to be a 'good solvent' in light of the scaling.

Fig. 2. shows the effect of solvent composition on the Λ of the polyelectrolyte solution at a constant temperature (298.15K) and at any given polyelectrolyte concentration. From the figure it is clear that an increase in the DMSO content in the solvent system leads to a decrease in Λ values and the calculated values are also in very good agreement with the experimental values.

Calculation of f in light of the Scaling theory

To use scaling theory to conductivity data analysis, the sizes of the correlation (ξ_0) as well as the electrostatic (ξ_e) blobs must be determined as they appear in the theoretical model (Eq1). These parameters are influenced by the solvent quality and are defined differently depending on whether the solvent behaves as a good or poor solvent for the polyelectrolyte. For poor solvents, where the solvent quality leads to a more collapsed polymer structure, the sizes of the blobs are given by the following relationships [14]

$$\xi_e = b\left(\frac{A^2}{\xi}\right)^{\frac{1}{3}} \quad (4)$$

$$\xi_o = (cb)^{-\frac{1}{2}}\left(\frac{A^2}{\xi}\right)^{\frac{1}{3}} \quad (5)$$

ξ is the dimensionless linear charge density parameter, given by (Manning 1972 [30]; Manning 1975) [31]

$$\xi = \frac{e^2}{\epsilon k_B T b} \quad (6)$$

where e = electrical elementary charge, ϵ = solvent relative permittivity, k_B = Boltzmann constant, T = temperature in absolute scale, b = contour distance per unit charge on polyion chain.

In contrast, for good solvents, where the polymer adopts an expanded conformation, the blob sizes are given by:

$$\xi_e = b\left(\frac{A^2}{\xi}\right)^{\frac{3}{7}} \quad (7)$$

$$\xi_o = (cb)^{-\frac{1}{2}}\left(\frac{A^2}{\xi}\right)^{\frac{1}{7}} \quad (8)$$

For the NaCMC - DMSO-water ternary solutions studied here, the good solvent conditions provide an excellent fit to the experimental data. This is likely due to the nature of DMSO as a solvent that promotes the more expanded polymer configurations, facilitating better ion mobility and

interaction with the solvent. The values of *f* calculated using the scaling approach for good solvents from the best-fit of the experimental equivalent conductances of the NaCMC - DMSO-water ternary solutions as well as the corresponding standard deviations (σ) are given in Table 2. The data shows that 41-45% of the counterions remain dissociated in solutions and the high standard deviations seen here can be attributed to the dependence of *f* on the polyelectrolyte concentration.

Following the method first employed by Sharma et al. (2013) [19] the value of *f* has been calculated with the help of equation 2 along with equations 6 and 7 which gives a quantitative description of the dependence of *f* on the polyelectrolyte concentration. The results are graphically represented to show the variation of *f* with polyelectrolyte concentration at different temperatures but constant solvent composition (Fig. 3.) and at different solvent compositions but at constant temperature (Fig. 4.). These results are discussed in the next section.

Influence of temperature, relative permittivity and polyelectrolyte concentration on counterion condensation

The fraction of uncondensed counterions (*f*) is a critical parameter that elucidates the phenomena of counterion condensation in polyelectrolyte solutions. Fig. 3. and 4. illustrate how (*f*) varies with $\sqrt{c_p}$ in DMSO-water solvent system containing 10%, 20%, 30%, and 40% DMSO by mass at the aforementioned temperatures. From both these figures it is clear that with an increase of NaCMC concentration there is a steady decrease in *f*. This trend indicates that more counterions are condensing onto the polyion chains at higher polymer concentrations. This behaviour is expected because as the concentration of NaCMC increases, the likelihood of electrostatic interactions between polyions and counterions also rises. This leads to a greater degree of counterion condensation, which effectively reduces the number of free counterions in the solution.

The increase in *f* observed with increasing temperature (Fig. 3.) at constant solvent composition and polyelectrolyte composition signifies that the quantity of thermal energy accessible for overcoming this electrostatic attraction between polyions and counterions will be able to release a larger fraction of the condensed counter ions to re-enter into the solution. This phenomenon indicates a reduction in the strength of polyion-counterion interactions at elevated temperatures, which is consistent with the observed increase in conductivity. It should also be noted that the relative permittivity decreases with increase in temperature which facilitates counterion

condensation on the polyion thus restricting the increase of *f* with temperature. The effect of temperature on the magnitude of *f* also highlights the dynamic nature of counterion condensation, where the balance between thermal energy and electrostatic forces dictates the degree of condensation [32].

Fig. 4. shows that at constant temperature, *f* decreases with an increase in DMSO mass fraction in the binary solvent system. This is also along expected lines because the lowering of relative permittivity of the solvent would increase the electrostatic forces of attraction thus facilitating the positively charged counterion condensation on the negatively charged polyion.

Comparison of our result obtained with similar studies shows that different systems behave differently and even qualitative similarity is not always observed [19,33,34]. Quantitative values differ significantly. The values of *f* for NaCMC - ethylene glycol - water ternary solutions varies between 67-76% [19], 49-66% for NaCMC - 2 butoxyethanol-water ternary solutions [34] as compared to 41-45% in this study. The low value of *f* in DMSO-water mixed solvent may be attributed to the unique structure of DMSO in water as described above.

Polyion equivalent conductivities

Fig. 5. and 6. illustrate how the polyion equivalent conductivities (Λ_p) of NaCMC vary with its concentration in DMSO-water mixtures with 10%, 20%, 30%, and 40% DMSO by mass at different temperatures. The results clearly reveal that similar to the changes observed with the fraction of uncondensed counterions, Λ_p also decreases with increasing NaCMC concentration in both the figures as expected. The increase in polyelectrolyte concentration leads to an interpenetration of the polyion chains leading to an entrapment of the counterions. The decrease in effective charge on the polyion leads to the coiling of the polyion chain which is a manifestation of increased counterion condensation leading to the decrease in Λ_p observed in Fig. 5. and 6. Similar observations were also observed by Bordi et al (2003) [33] and Das et al (2016) [34].

Fig. 5. shows that at constant solvent composition and c_p, Λ_p increases with increase in temperature though Fig. 3. depicts that the *f* decreases. This is due to the higher mobility of the polyions and counterions due to the desolvation of the sodium ions [35] and the polyion as well as the coiling of the polyion chain due to increased counterion condensation. Similar behaviour where

there is a lowering of the values of fraction of uncondensed counterions but increase in Λ_p was observed for NaCMC in 2-butoxyethal-water system [34]. In Fig. 6., it can be clearly seen that Λ_p decreases with increasing DMSO content in the solvent. Increasing DMSO content results in decreasing the dielectric constant of the medium resulting in increased condensation of the counterion (Fig. 3.) and hence decreased intrachain repulsion and coiling of the polyion chain leading to a decrease in Λ_p.

Association constant and the standard Gibb's free energy of association

Let K_A be the the equilibrium constant (or the association constant) for the condensation of the cation (sodium) counterions on the active site of the polyion. K_A is related to f by the following equation:

$$\ln K_A = [\ln (1-f)/f] - \ln (fc_p) \quad (9)$$

where c_p represents the concentration of the polyelectrolyte (Sharma et al 2013) [19].

The standard Gibbs free energy for the association reaction (ΔG_A^0) is given by the following equation:

$$\Delta G_A^0 = -RT \ln K_A \quad (10)$$

Fig. 7. and 8. show the variation of ΔG_A^0 with change in concentration of NaCMC in DMSO-water binary solutions containing 10%, 20%, 30%, and 40% DMSO by mass at different temperatures and at different solvent compositions respectively. From Fig. 3. we can see that as Na-CMC concentration increases, f decreases which implies that counterion condensation increases due to favourable counterion- polyion interactions leading to an increase in ΔG_A^0 values as is evident in both Fig. 7. and 8. The negative sign of ΔG_A^0 values mean the association reactions are spontaneous over the entire range of polyelectrolyte concentrations, temperatures and solvent compositions studied here.

ΔG_A^0 becomes slightly more negative with rising temperature, indicating that the interactions between polyions and counterions become only slightly favourable at higher temperatures. Increase in temperature leads changes in the solvent structure, as the increased thermal motion can lead to a breakdown of solvent-mediated interactions that contribute to the stability of the polyion-counterion complexes. On the other hand, increase in temperature leads to decrease in relative permittivity (Table 1) which is favourable for ion association. As a consequence of the interplay of these opposing factors it is observed that the counterion condensation process is only slightly

more favourable at higher temperatures as can be seen in Fig. 7. At higher polyelectrolyte concentration, figure 8 shows that with the increase in DMSO content in the solvent, ion association is markedly favourable due to strong counterion – polyion interaction due to decrease in relative permittivity.

Transference number of carboxymethylcellulose polyanion (T_p)

The ratio of the equivalent conductivity of the polyion (λ_p) and the polyelectrolyte (Λ) is defined as the transference number (T_p) which represents the fraction of the current carried by the polyion.

$$T_p = \frac{\lambda_p}{\Lambda} \qquad (11)$$

Fig. 9. and 10. presents the variation of transference number of carboxymethylcellulose anion with $\sqrt{c_p}$ at different temperatures and solvent compositions respectively. In both the figures a monotonous decrease in T_p with increase $\sqrt{c_p}$ is observed. For a given solvent composition and polyelectrolyte concentration, T_p always increases with increase in temperature which is in line with our observation that counterion condensation increases with increase in temperature (Fig. 3.) and decreases with increasing DMSO content (Fig. 10.) thus demonstrating increased cation dissociation from the polyion. Similar trends in T_p values were observed by Das et al (2014) [36] for Sodium polystyrene sulfonate in ethylene glycol – water mixed solvent system.

T_p greater than unity (hence negative values for transference numbers for counterions) were observed for solvent systems containing 10 and 20% by mass of DMSO (Fig. 10.). This implies that a substantial amount of sodium cations is condensed onto the polyion chains and move along with them towards the negative terminal. In fact, T_p values greater than unity is considered to be a characteristic property of polyelectrolytes and such accounts are available in literature [37-39] to name a few.

The coefficient of friction between the polyion and the solvent system

Kuznetsov et al 1990 have proposed an expression (equation 12) to estimate the coefficient of friction between a polyion monomer unit and the solvent system (f_{ps}) [39]

$$f_{ps} = \frac{|z_p| f F^2}{\lambda_p} \qquad (12)$$

where z_p is the number of primary charges on the entirely dissociated polyion monomer unit and the other symbols have been described earlier.

Fig. 11. and 12. depicts the increase in f_{ps} with increasing $\sqrt{c_p}$ (where c_p is the NaCMC concentration) and also with decrease in temperature and increase in DMSO content of the solvent system respectively. There are three factors affecting f_{ps} and they are the coefficient of viscosity of the medium, size and mobility of the polyion. With the increase in DMSO content in the solvent system, the coefficient of viscosity increases whereas the size and mobility may decrease due to counterion condensation. Fig. 12. shows that there is a net increase in the f_{ps} with increasing DMSO content in the system thus indicating that the influence of the increase in viscosity is much greater than the other two factors. Fig. 11. shows that f_{ps} decreases with increase in temperature. Increase in temperature leads to lowering of coefficient of viscosity (Table 1) as well as increased counterion condensation (Fig. 3.) leading to decreased size due to the coiling of polyion chain causing f_{ps} to decrease with rise in temperature.

5. Conclusion

In the current work, electrical conductivity of the solutions of the polyelectrolyte NaCMC in DMSO-water mixed solvent containing 10, 20, 30 and 40 percent DMSO by mass at 298.15, 303.15, 308.15 and 313.15 K were carried out under salt free conditions as a function of polyelectrolyte concentration. The equivalent conductance was found to decrease with increasing polyelectrolyte concentration in all cases. Using the scaling model as proposed by Colby et al containing the adjustable parameter *f* the experimental conductivity data was analysed considering a semi dilute concentration regime using good solvent correlations. The results obtained for the fraction of uncondensed counterions, polyion equivalent conductances, standard Gibb's free energy for counterion condensation, transference number of polyion and the coefficient of friction between polyion and solvent have been explained on the basis of counterion-polyion interactions under various conditions. These results are found to be qualitatively in line with similar studies of other systems available in literature.

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Table 1 The physical properties, including density, viscosity, and dielectric constant of dimethyl sulfoxide (DMSO)-water mixtures containing 10%, 20%, 30%, and 40% DMSO by mass were measured at varying temperatures under a pressure of 0.1 MPa.

T/K	ρ_0 / g·cm^{-3}		η_0 / mPa·s		λ_c^0 / Scm^2mol^{-1}	ε [a]
	Current work	lit.	Current work	lit.		
			w_1 = 0.10			
298.15	1.0098	1.00971[b]	1.0656		43.17	77.64
303.15	1.0083		0.9681		47.96	76.04
308.15	1.0073	1.00613[b]	0.8571		52.29	74.45
313.15	0.9987		0.7457		57.60	72.94
			w_1 = 0.20			
298.15	1.0242	1.0242[c]	1.3406		40.43	76.58
303.15	1.0189	1.0197[c]	1.2121		44.36	75.02
308.15	1.0132	1.0152[c]	1.0545		48.97	73.49
313.15	1.0107	0.9984[c]	0.9081		53.34	72.02
			w_1 = 0.30			
298.15	1.0393		1.7145		40.22	75.35
303.15	1.0342		1.5621		43.52	73.84
308.15	1.0285		1.3972		47.43	72.36
313.15	1.0211		1.2420		51.39	70.93
			w_1 = 0.40			
298.15	1.0532	1.0535[c]	2.2018		38.83	73.81
303.15	1.0511	1.0525[c]	1.9912		42.67	72.38
308.15	1.0450	1.0453[c]	1.7903		46.32	70.97
313.15	1.0329	1.0401[c]	1.5917		50.05	69.59
			w_1 = 1.00			
298.15	1.0948	1.0952[d]	2.0182	2.021[d]		
303.15	1.0892	1.0902[d]	1.8387	1.843[d]		
308.15	1.0851	1.0853[d]	1.7075	1.710[d]		
313.15	1.0797	1.0803[d]	1.5192	1.525[d]		

Standard uncertainties *u are* $u(T) = 0.05$ K, $u(w) = 0.01$ and combined expanded uncertainties U_c are $u_c(\rho_0)$ = 0.00005 $\mathrm{g \cdot cm^{-3}}$, and $u_c(\eta_0)$= 0.00015 $\mathrm{mPa \cdot s}$ (0.95 level of confidence).

[a] Calculated with the equations as described in the ref [26]. [b] from ref [27]. [c] from ref [28].[d] from ref [23].

Table 2 The fractions of free counterions (*f*) calculated from the best-fit of the experimental equivalent conductances for NaCMC in DMSO-water mixed solvent media using the scaling theory for good solvent correlation as well as the respective standard deviations (σ).

T/K	Mass % of DMSO	*f*	σ
298.15	10	0.45	1.9
303.15	10	0.44	2.0
308.15	10	0.43	2.0
313.15	10	0.42	2.1
298.15	20	0.44	1.7
303.15	20	0.43	1.8
308.15	20	0.43	1.8
313.15	20	0.42	1.9
298.15	30	0.43	1.4
303.15	30	0.42	1.5
308.15	30	0.42	1.6
313.15	30	0.42	1.6
298.15	40	0.43	1.2
303.15	40	0.42	1.3
308.15	40	0.42	1.4
313.15	40	0.41	1.4

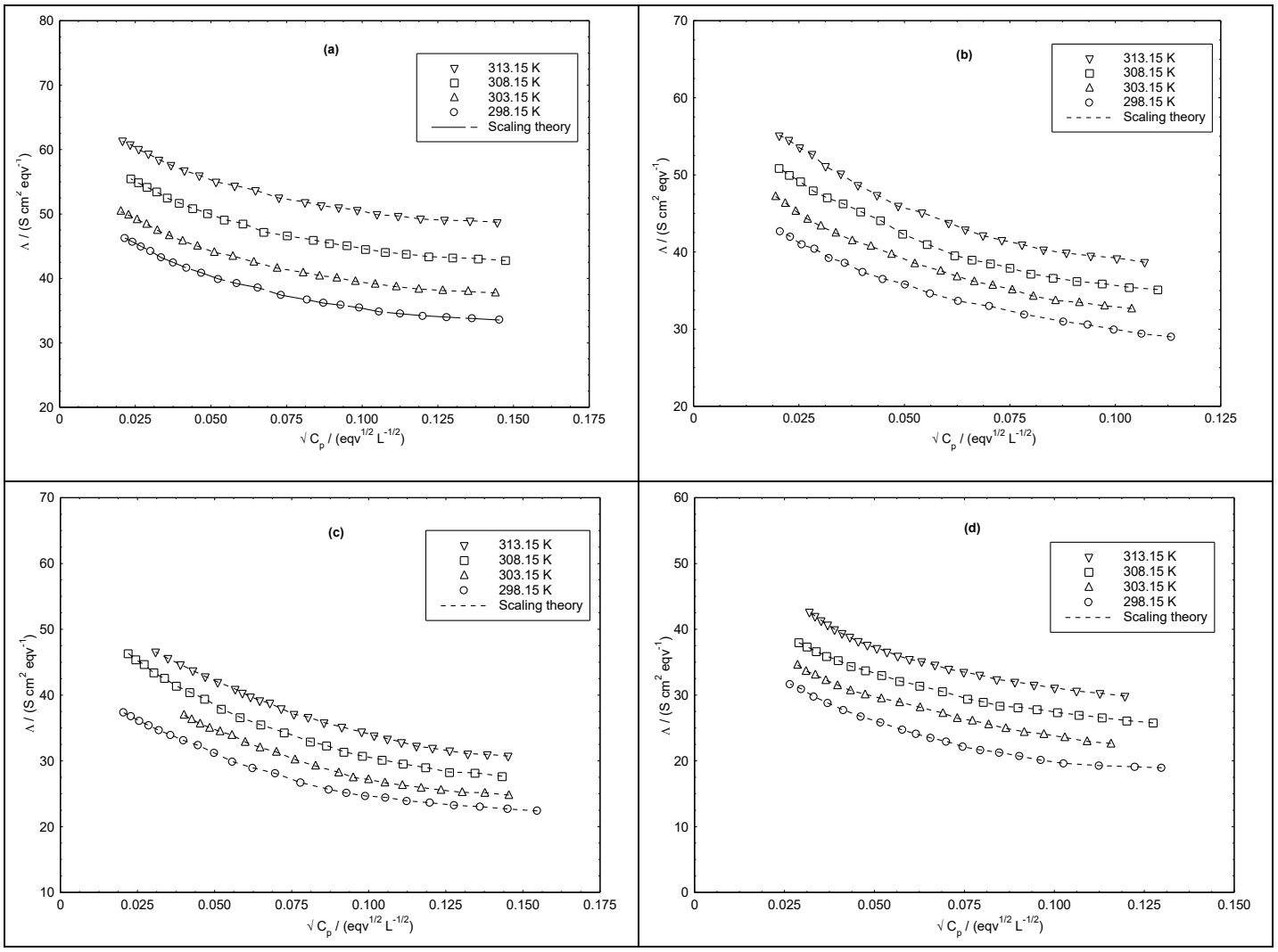


Fig. 1 Concentration dependence of the equivalent conductivities (Λ) of sodium carboxymethylcellulose in DMSO-water mixed solvent media containing (a) 10 mass percent, (b) 20 mass percent, (c) 30 mass percent, and (d) 40 mass percent of DMSO at different temperatures. Predicted values according to scaling theory using good solvent correlation: dashed lines.

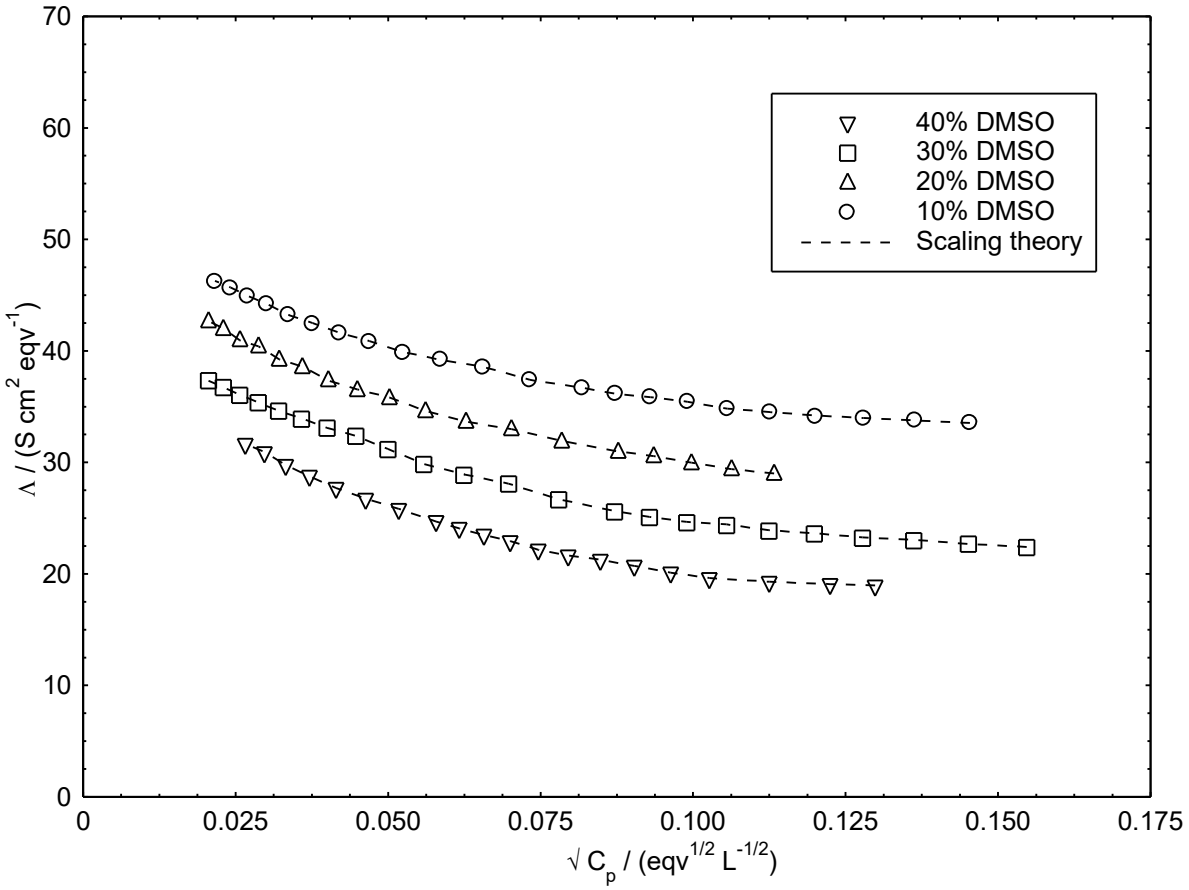


Fig. 2 Concentration dependence of the equivalent conductivities (Λ) of sodium carboxymethylcellulose in different DMSO-water mixed solvent media (containing 10, 20, 30, and 40 mass percent of DMSO) at 298.15 K. Predicted values according to scaling theory using good solvent correlation: dashed lines.

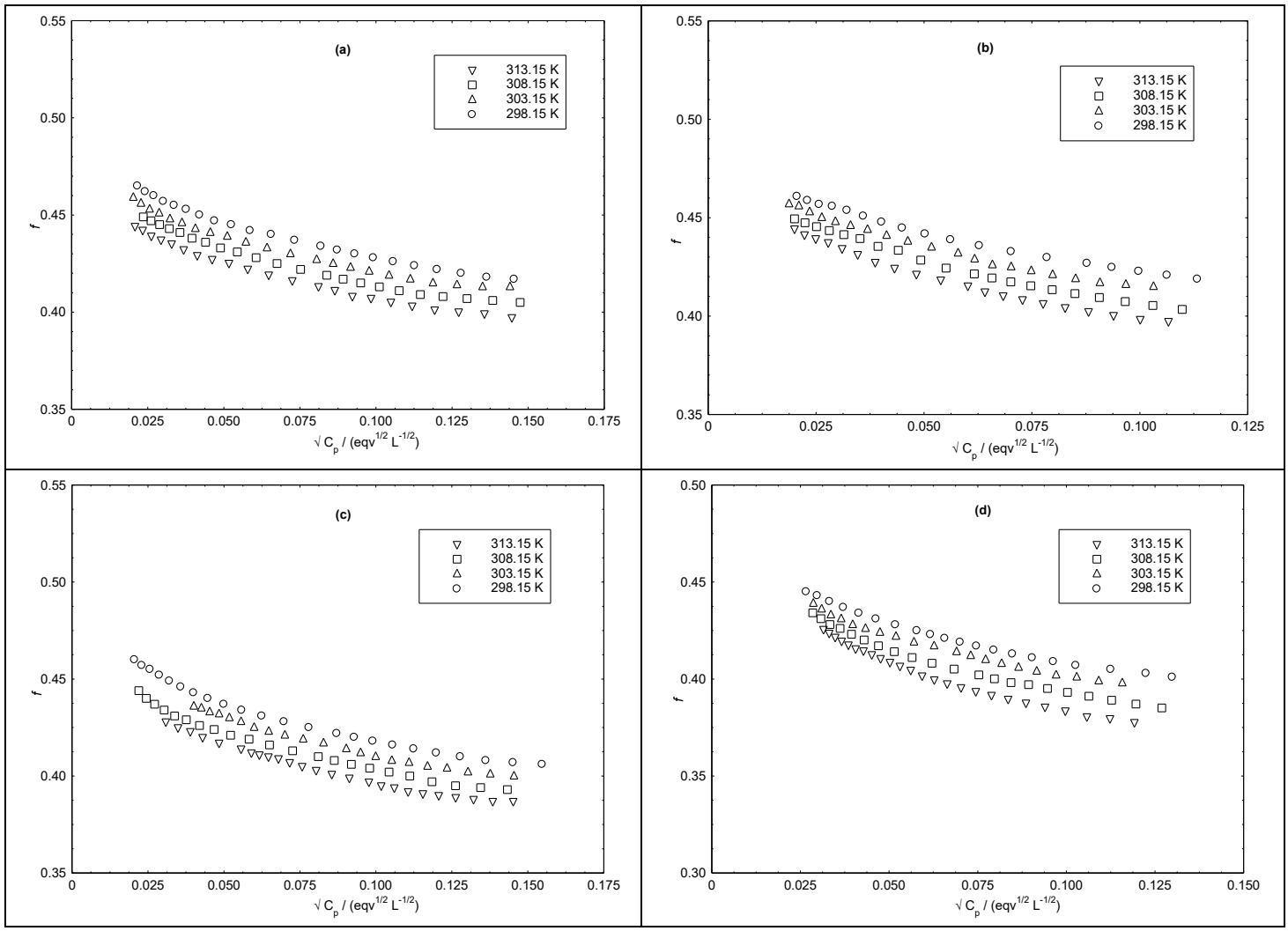


Fig. 3 Variation of the fraction of uncondensed counterions (*f*) of sodium carboxymethylcellulose in DMSO-water mixed solvent media containing (a) 10 mass percent, (b) 20 mass percent, (c) 30 mass percent, and (d) 40 mass percent of DMSO at different temperatures.

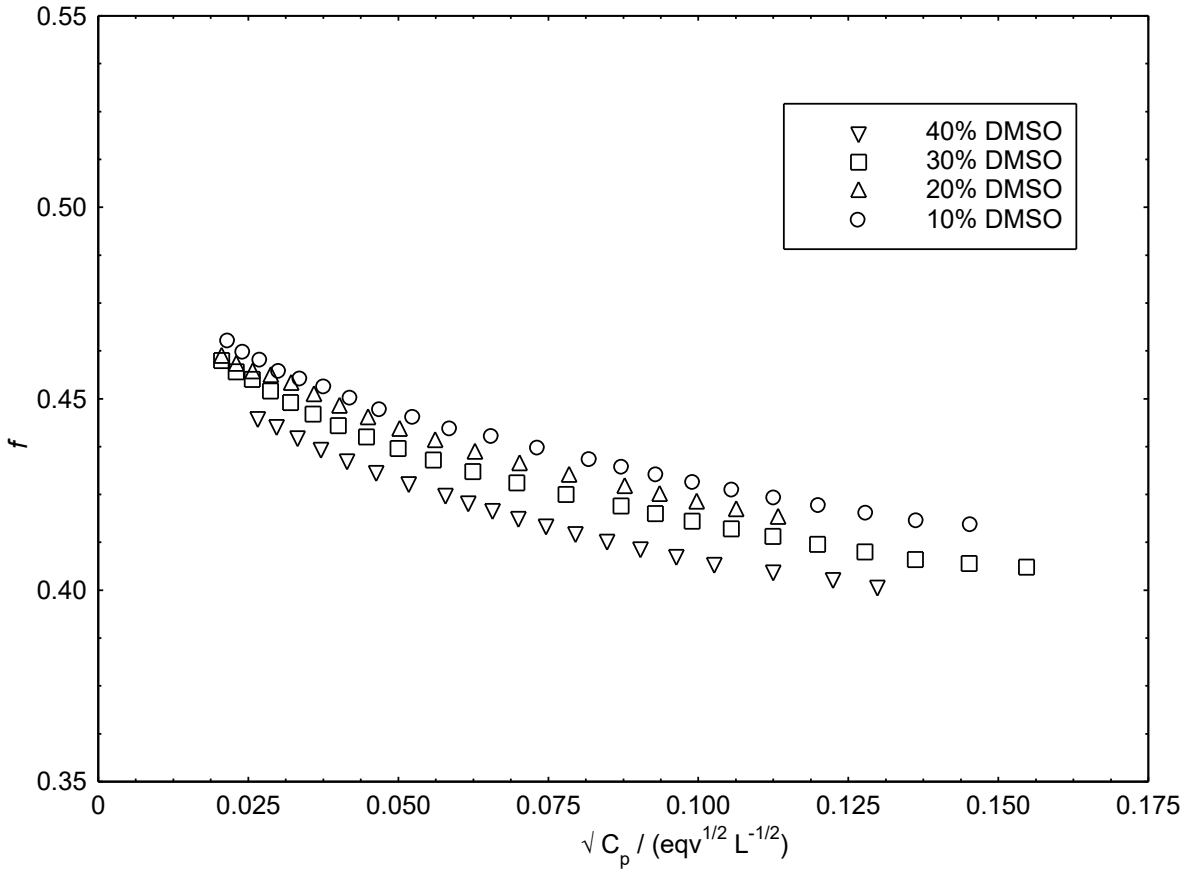


Fig. 4 Variation of the fraction of uncondensed counterions (*f*) of sodium carboxymethylcellulose in different DMSO-water mixed solvent media (containing 10, 20, 30, and 40 mass percent of DMSO) at 298.15 K.

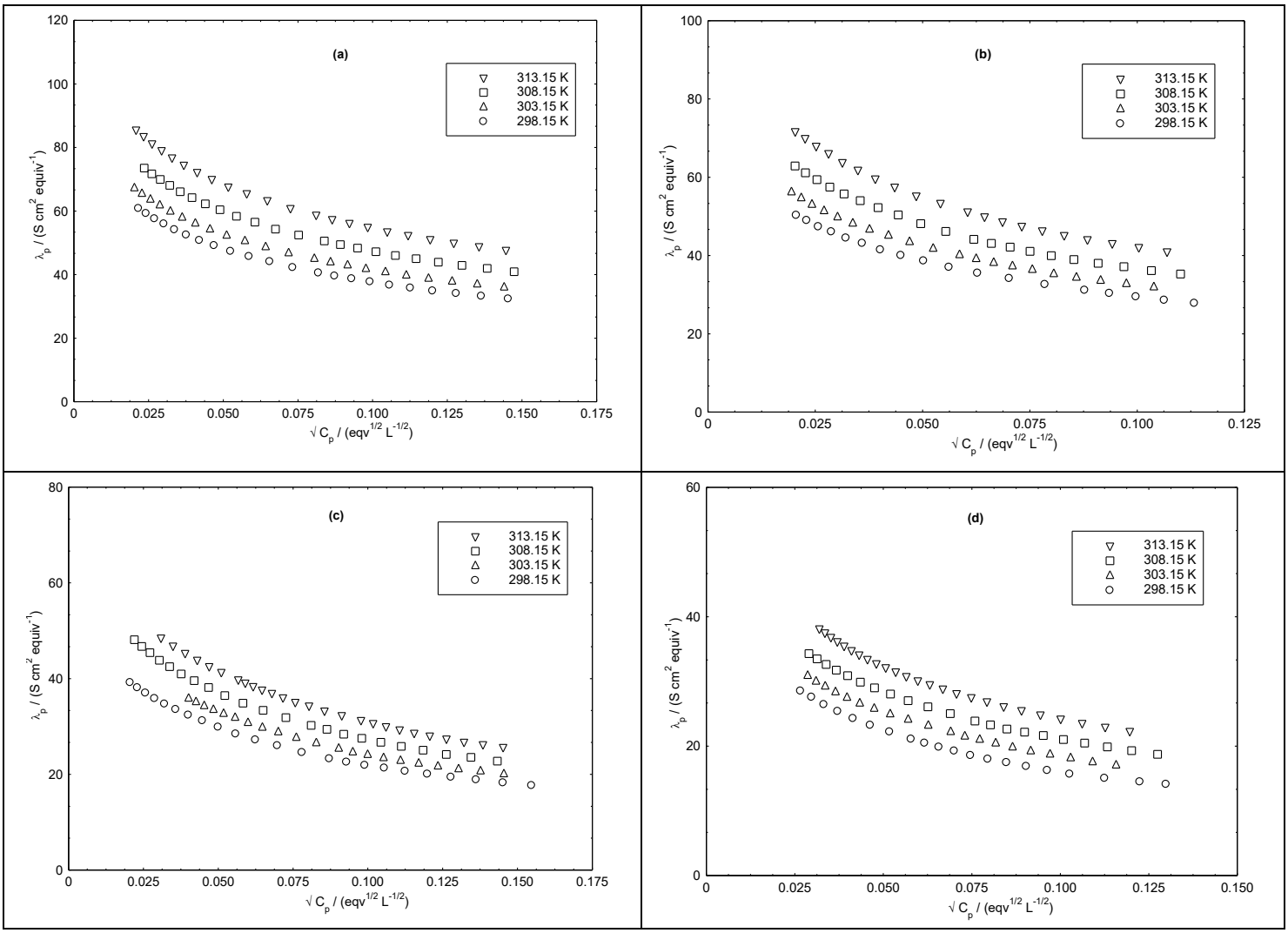


Fig. 5 Concentration dependence of the polyion equivalent conductivities (λ_p) of sodium carboxymethylcellulose in DMSO-water mixed solvent media containing (a) 10 mass percent, (b) 20 mass percent, (c) 30 mass percent, and (d) 40 mass percent of DMSO at different temperatures.

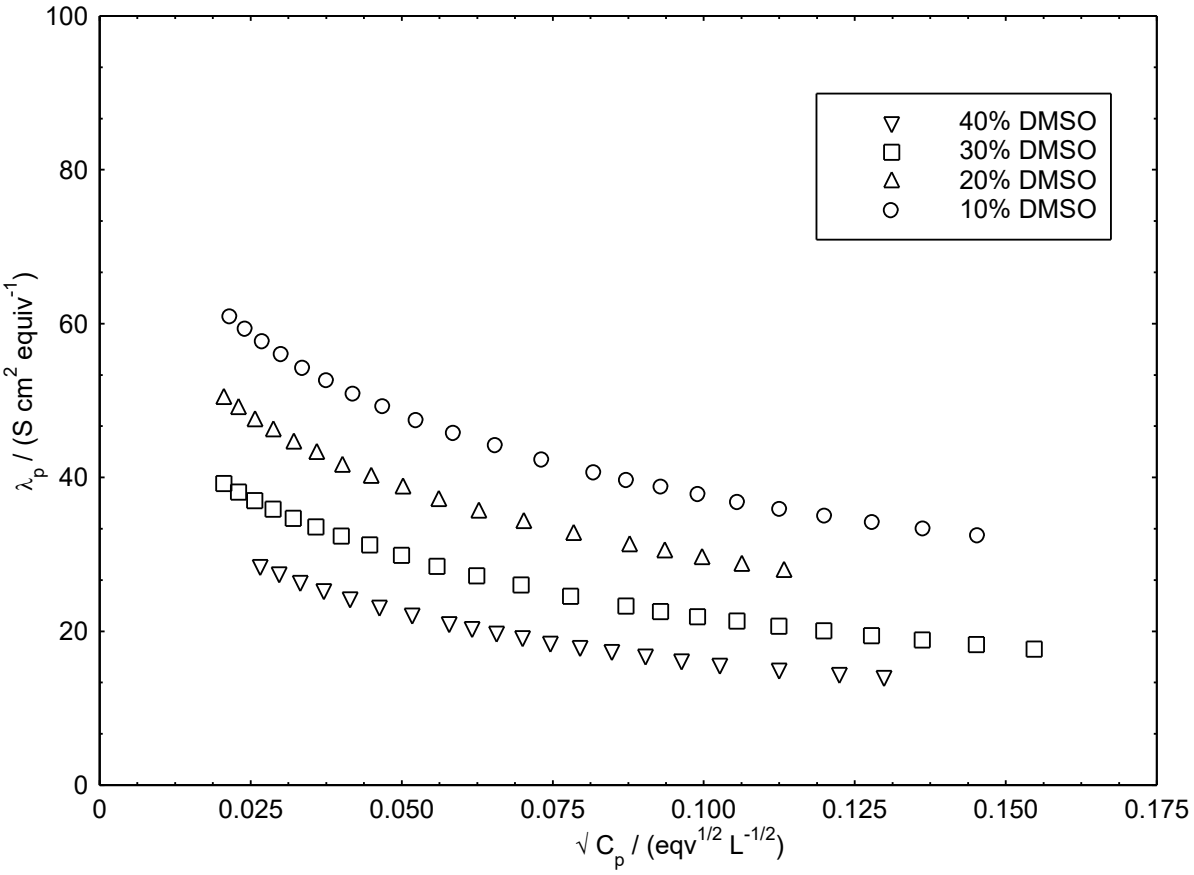


Fig. 6 Concentration dependence of the polyion equivalent conductivities (λ_p) of sodium carboxymethylcellulose in different DMSO-water mixed solvent media (containing 10, 20, 30, and 40 mass percent of DMSO) at 298.15 K.

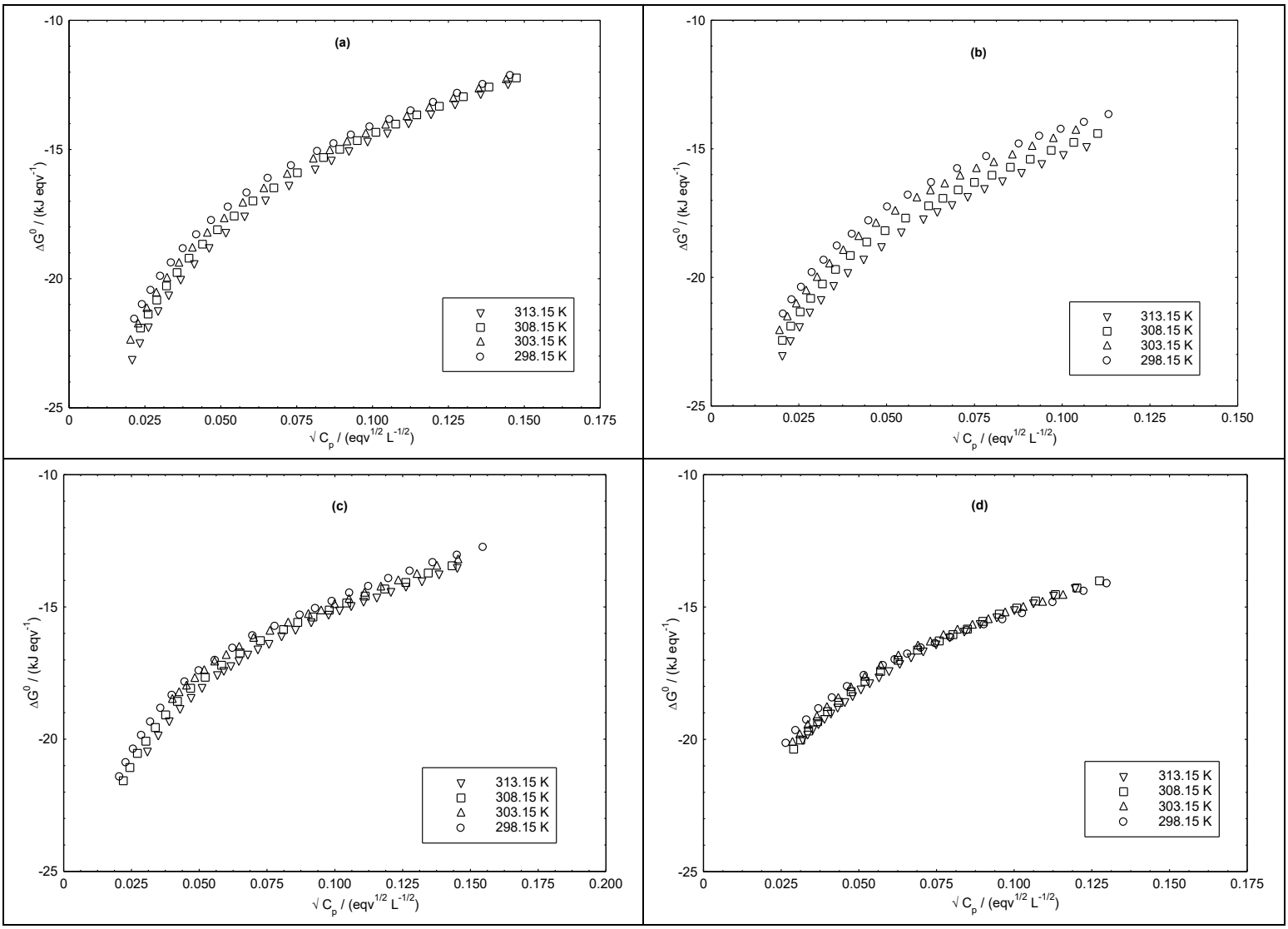


Fig. 7 Concentration dependence of the standard state free energy change ($\Delta G_{\mathrm{A}}^{0}$) of sodium carboxymethylcellulose in DMSO-water mixed solvent media containing (a) 10 mass percent, (b) 20 mass percent, (c) 30 mass percent, and (d) 40 mass percent of DMSO at different temperatures.

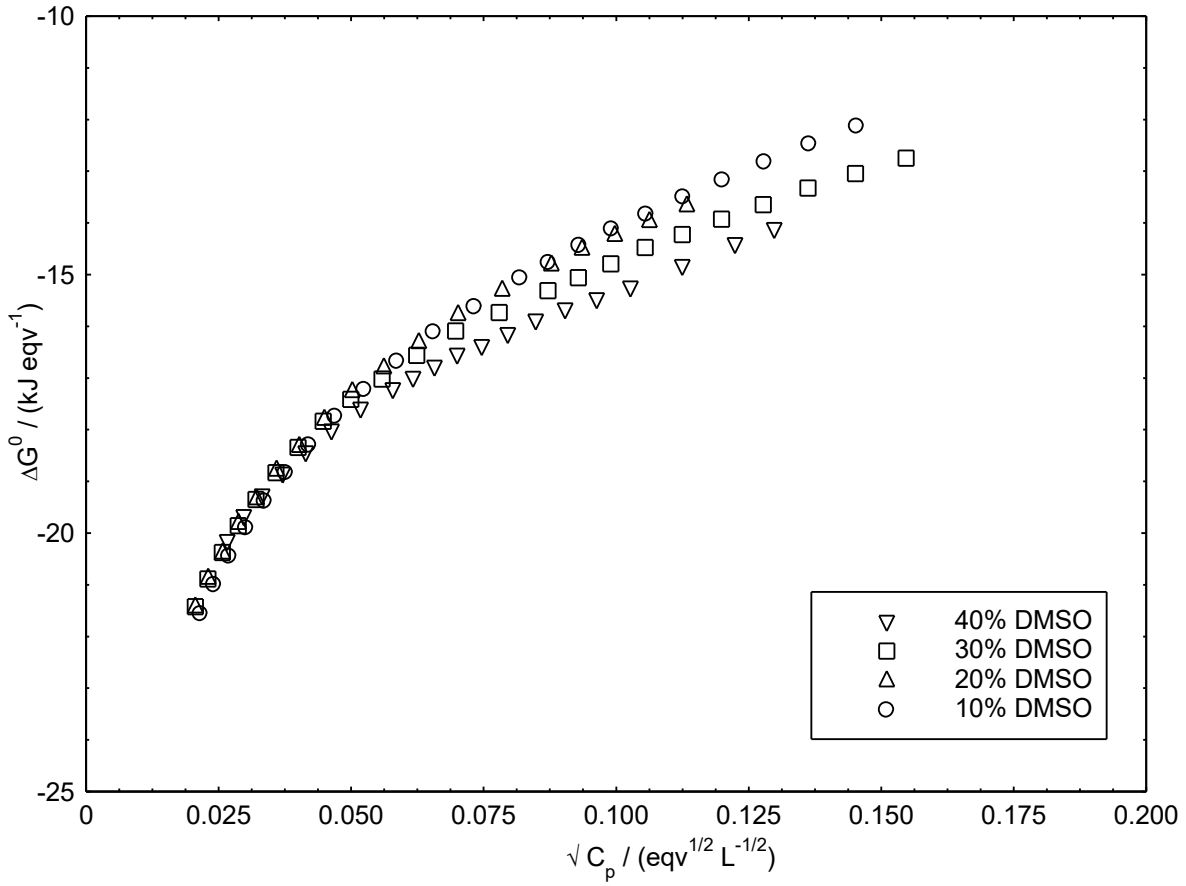


Fig. 8 Concentration dependence of the standard state free energy change ($\Delta G_{\mathrm{A}}^{0}$) of sodium carboxymethylcellulose in different DMSO-water mixed solvent media (containing 10, 20, 30, and 40 mass percent of DMSO) at 298.15 K.

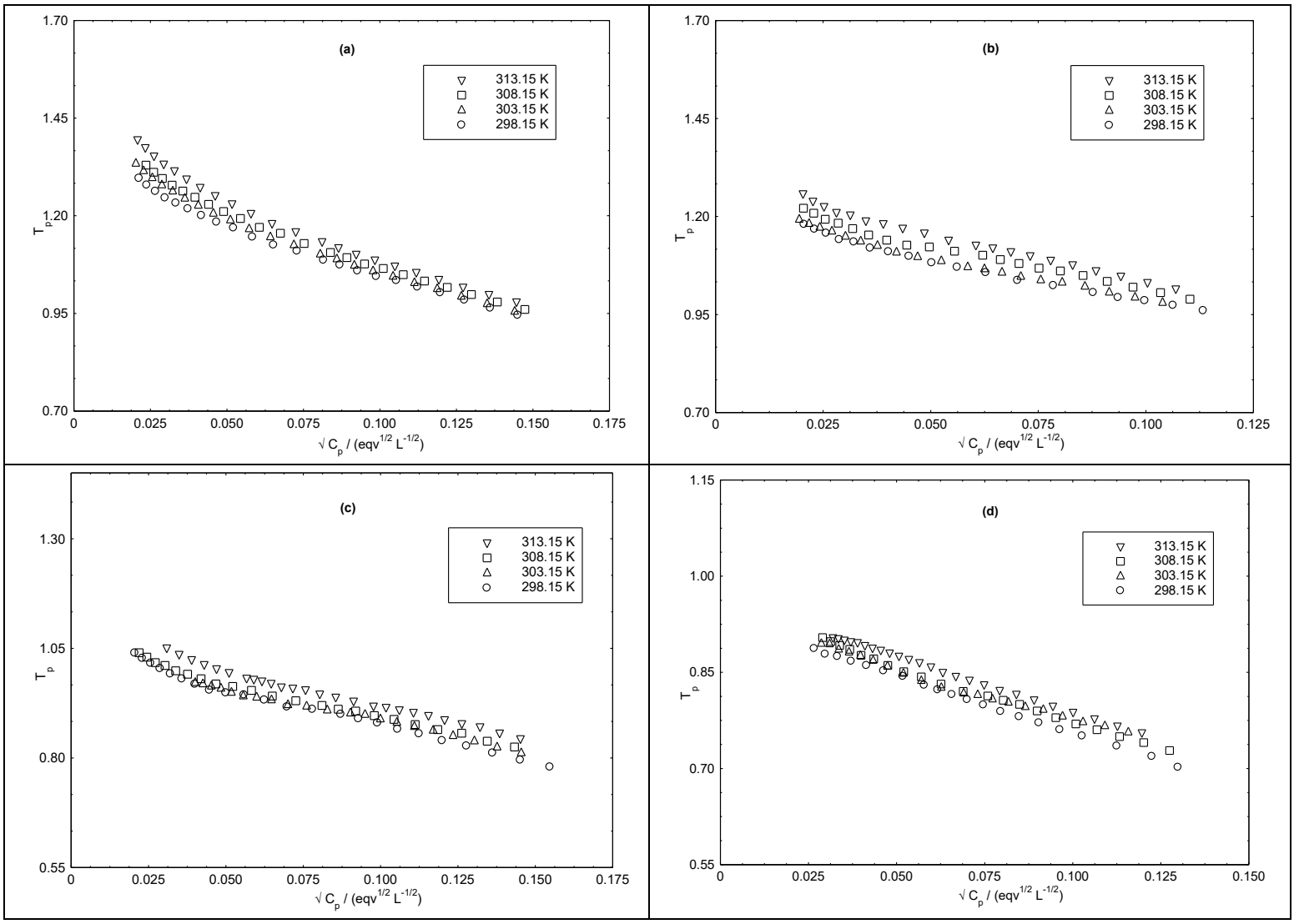


Fig. 9 Concentration dependence of the transference number (T_p) of carboxymethylcellulose ion in DMSO-water mixed solvent media containing (a) 10 mass percent, (b) 20 mass percent, (c) 30 mass percent, and (d) 40 mass percent of DMSO at different temperatures.

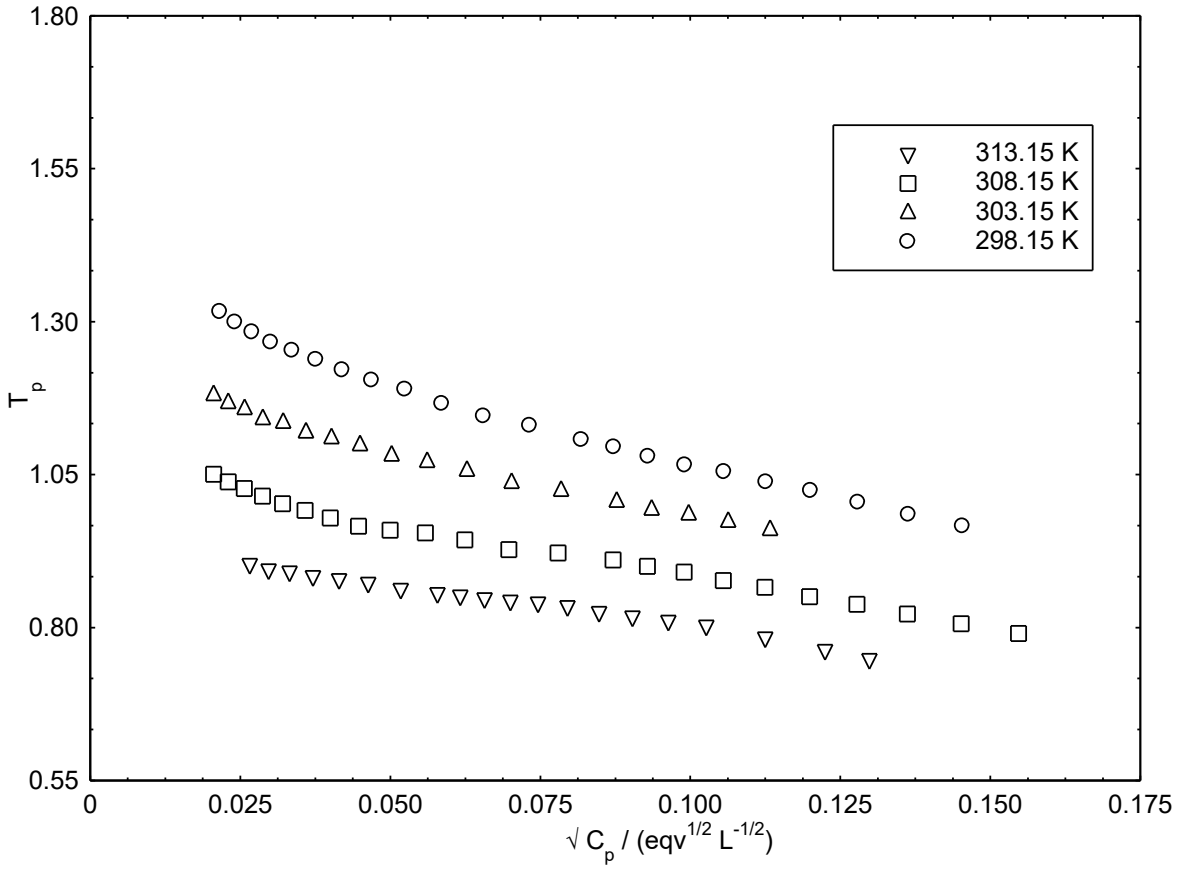


Fig. 10 Concentration dependence of the transference number (T_p) of carboxymethylcellulose ion in different DMSO-water mixed solvent media (containing 10, 20, 30, and 40 mass percent of DMSO) at 298.15 K.

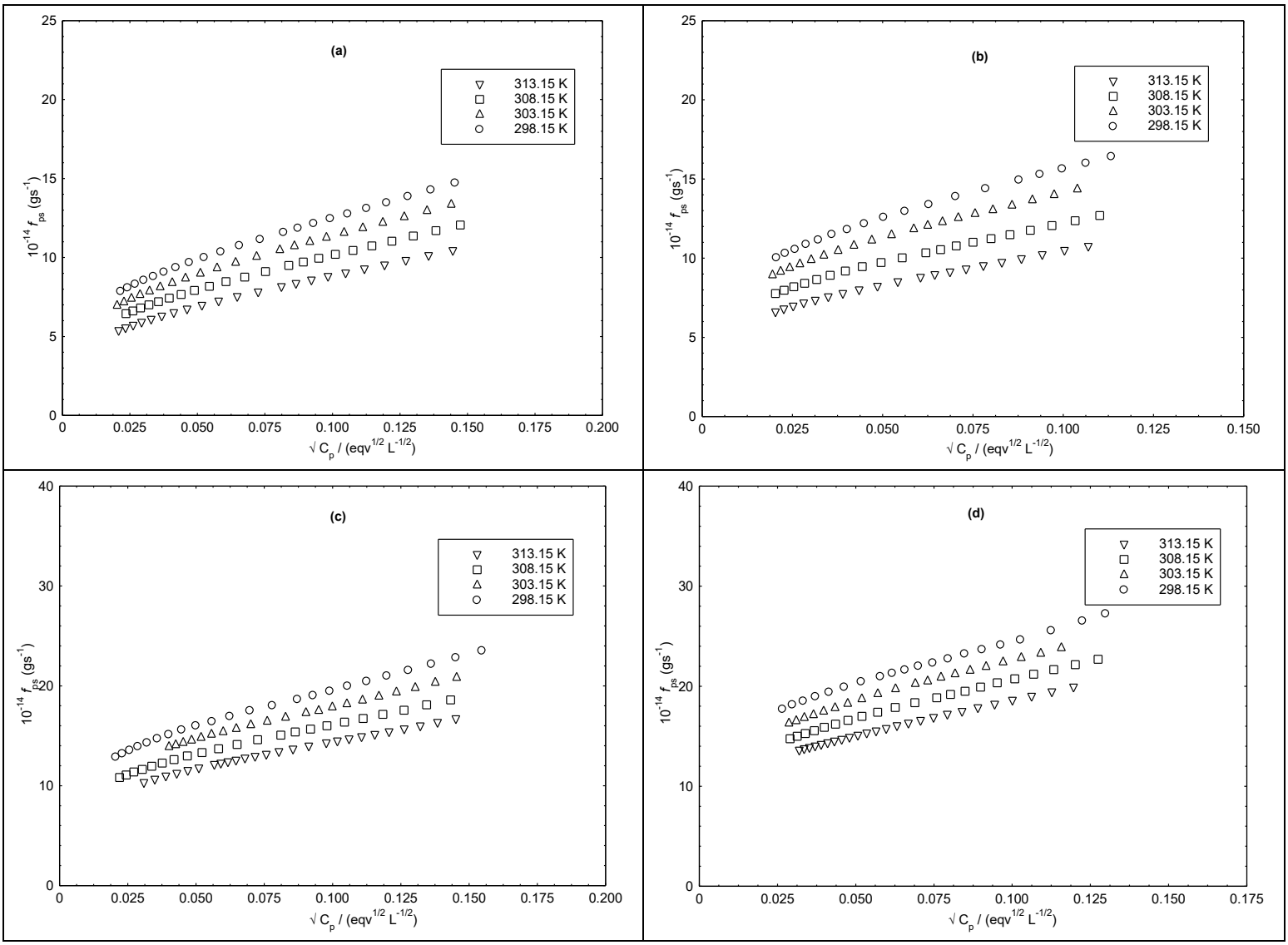


Fig. 11 Concentration dependence of the coefficient of friction between carboxymethylcellulose ion and the solvent (f_{ps}) in DMSO-water mixed solvent media containing (a) 10 mass percent, (b) 20 mass percent, (c) 30 mass percent, and (d) 40 mass percent of DMSO at different temperatures.

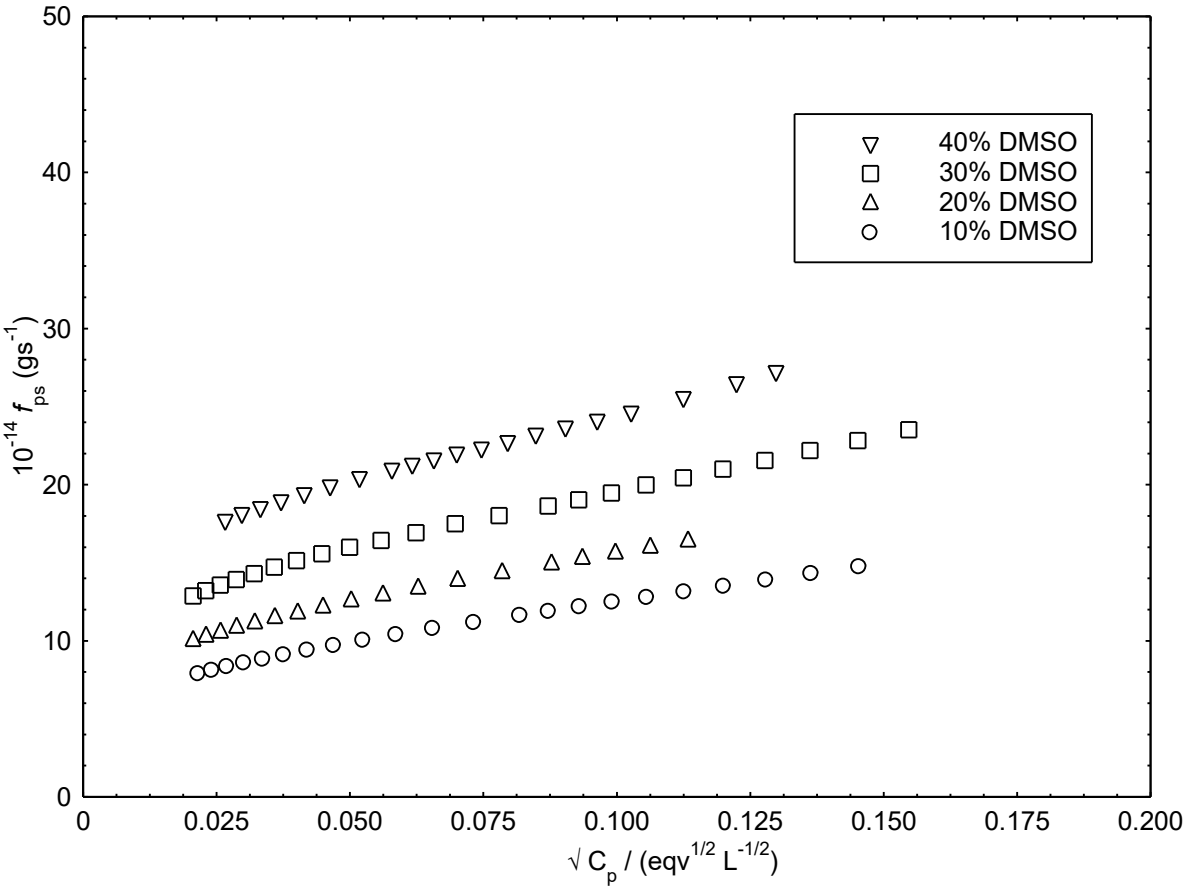


Fig. 12 Concentration dependence of the coefficient of friction between carboxymethylcellulose ion and the solvent (f_{ps}) in different DMSO-water mixed solvent media (containing 10, 20, 30, and 40 mass percent of DMSO) at 298.15 K.