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Temperature Effect on Transference Numbers for KCl in Ethanol–Water Mixtures

Masakatsu UENO,* Shōgo I, and Kiyoshi SHIMIZU
Department of Applied Chemistry, Faculty of Engineering, Doshisha University, Karasuma Imadegawa, Kamigyo-ku, Kyoto 602
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Cation-transference numbers were determined by the moving boundary method for 0.02 mol dm^{-3} KCl in 5-, 10-, 15-, 20-, and 30 mol% ethanol-water mixtures at 15 and 35 °C. The cation-transference number has a maximum around 10 mol% of ethanol at each temperature studied, and becomes larger with decreasing temperature in the solvent of the same composition. From the temperature dependence of the transference number, the differences in the activation energy of transport between K^+ and Cl^- ions were estimated, and it was found that the activation energy of the K^+ ion is less than that of the Cl^- ion and the difference becomes larger in the range of 5—20 mol% of ethanol. These results are discussed in terms of structural effects and ion-solvent interactions.

Transference number measurement is a matter of considerable importance in the study of electrolyte solutions by the conductivity method since individual ionic conductances can be determined without any assumptions by combining transference numbers with electrolyte conductances. Such a single-ion property at infinite dilution is closely related to the ion-solvent interaction. The investigation of the temperature and pressure dependence of limiting ionic conductances and correlated quantities in water has led to the important concept on the ion-solvent interaction in relation to the unique structure properties of water.[1–4] Since a small addition of alcohols to water increases the degree of structure of solution,[5] it is interesting to measure the transference numbers and conductances of electrolytes in these mixtures as a function of temperature and pressure. However, a few papers have been published for the temperature[6] and pressure[7] effects on transference numbers in alcohol–water mixtures. In a previous paper,[7] we reported transference numbers for KCl in ethanol–water mixtures up to 30 mol% of ethanol under high pressure at 25 °C and discussed specific interactions between the ions and solvent. Here the temperature effect on transference numbers for KCl in ethanol–water mixtures is reported.

Experimental

Potassium chloride of high purity was obtained from Merck and dried above 130 °C prior to use. Purification of ethanol and water was the same as described before.[7] The solutions of 0.02 mol dm^{-3} KCl were prepared by weighing on the assumption that the densities of the solutions were equal to those of the solvent.[8]

Cation-transference numbers t_+ were determined by the autogenic moving-boundary method using a cadmium anode and a silver–silver chloride cathode. The velocity of the moving boundary formed by KCl and $CdCl_2$ solutions was detected by measuring a change in resistance between two platinum probe electrodes. The volume between the probe electrodes was determined by calibration runs at each temperature using 0.02 mol dm^{-3} KCl aqueous solution and the values of $t_+=0.4924$ at 15 °C and 0.4885 at 35 °C by Allgood *et al.*[9] The calibrated volume had a standard deviation better than 0.2%. Details of cell construction, other apparatus, and the procedure for calculating the apparent and final transference numbers have been described previously.[7]

Results and Discussion

The cation-transference numbers t_+ obtained are listed in Table 1. The variation of t_+ with the ethanol content is similar at various temperatures studied as seen in Fig. 1. The cation-transference number initially increases up to about 10 mol% of ethanol and then decreases. The characteristic features for the temperature effect on t_+ are the following: The cation-transference number in the solvent of the same composition becomes larger at lower temperature, and the initial increase and the following decrease in t_+ with increasing ethanol content become more rapid with decreasing temperature. These features will be maintained for the limiting cation-transference number t_+° since there is very little concentration dependence in t_+ in the case of t_+ which is close to 0.5 as shown by the following Kay-Dye equation:[10]

$$t_+^\circ = t_+ + (0.5 - t_+)\Lambda_e/\Lambda^\circ, \tag{1}$$

where Λ_e is the electrophoretic contribution to conductance and Λ° is the limiting molar conductance of KCl. In Fig. 1, the data at 5 °C by Erdey-Grúz and Majthényi[6] are also shown. The initial increase in

TABLE 1. CATION-TRANSFERENCE NUMBERS FOR 0.02 mol dm^{-3} KCl IN ETHANOL–WATER MIXTURES AT 15-, 25-,[a] AND 35 °C

t	Mol% of ethanol					
°C	0[b]	5	10	15	20	30
15	0.4924	0.5078(6)[c]	0.5137(4)	0.5099(5)	0.5053(4)	0.4879(6)
25	0.4901	0.5025(4)	0.5060(7)	0.5052(6)	0.5004(5)	0.4856(5)
35	0.4885	0.4976(6)	0.5014(5)	0.4986(7)	0.4933(7)	0.4809(7)

a) Ref. 7. b) Ref. 9. c) The numbers in parentheses are 10^4 times the standard deviation of repeated runs.

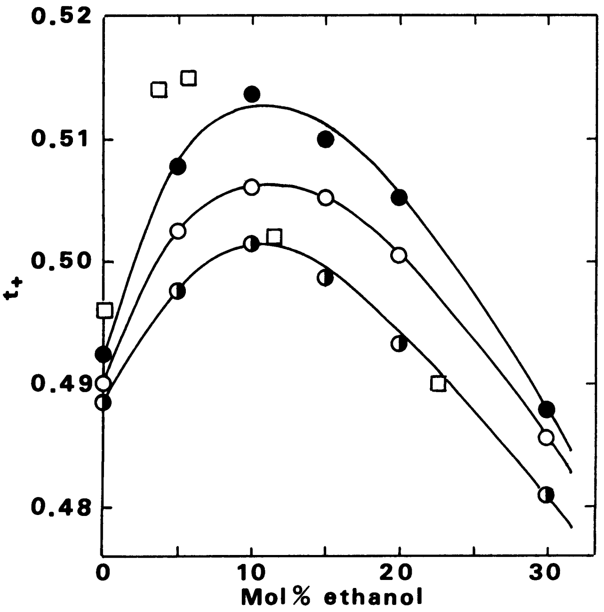

Fig. 1. Variation of the transference number for the K^+ ion with mol% of ethanol at various temperatures. ●: 15 °C, ○: 25 °C, ◑: 35 °C, □: 5 °C, Ref. 6.

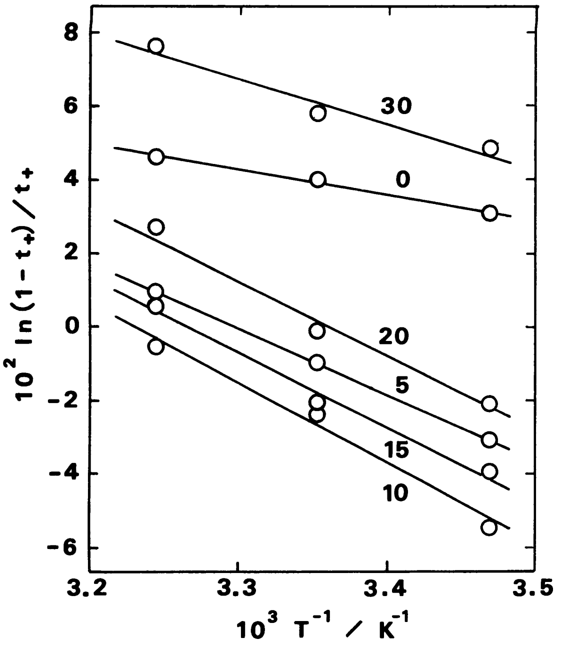

Fig. 2. A logarithmic plot of the ratio of anion- to cation-transference number against the reciprocal of the absolute temperature. Mol% of ethanol is shown in the plot.

t_+ at 5 °C is larger than that at 15 °C obtained by us, although the values above 10 mol% of ethanol at 5 °C in Ref. 6 appear to be fairly small just as those at 25 °C.

In the previous paper,[7] it has been shown that the Zwanzig dielectric friction theory[11] could not account for the variation of the transference number with the ethanol content. One of the reasons for it could be due to the neglect of the delicate difference in the ion-solvent interaction between K^+ and Cl^- ions although it is considered from a wide variety of thermodynamic and transport data that the influence of K^+ and Cl^- ions on the solvent structure is similar and almost equal in magnitude: The B-coefficients of the viscosity for K^+ and Cl^- ions were assumed to be equal in water.[1] However, the variation of the transference number with solvent composition as well as temperature and pressure sensitively reflects the relative difference in the ion-solvent interaction between these ions.

The slope of $\ln(1-t_+^\circ)/t_+^\circ$ plotted against the reciprocal of the absolute temperature $1/T$ should yield the difference in the activation energy of transport between K^+ and Cl^- ions at infinite dilution. Figure 2 shows such a plot where the concentration dependence of the transference number is neglected. The difference in the activation energy, $E(\mathrm{K}^+)-E(\mathrm{Cl}^-)$, was roughly estimated by assuming the linearity between $\ln(1-t_+)/t_+$ and $1/T$. The values obtained in 0-, 5-, 10-, 15-, 20-, and 30 mol% of ethanol are −0.6, −1.5, −1.8, −1.7, −1.7, and −1.0 kJ mol^{-1}, respectively: The activation energy for the K^+ ion is less than that for the Cl^- ion and the difference becomes larger in the water-rich region, 5—20 mol%. In ethanol-water mixtures, selective solvation would arise. It is considered that both the K^+ and the Cl^- ions interact more strongly with water molecules than with ethanol molecules because the dipole moment of a water molecule is larger than that of an ethanol molecule. The ion-solvent interaction of the Cl^- ion also involves the additional contribution of a hydrogen bond with water molecules.[12] In ethanol–water mixtures, the interaction of the Cl^- ion with water molecules would be weaker than in pure water, while that of the K^+ ion with water molecules would be stronger because of the enhanced basicity of water molecules.[13] Therefore, the radius of the solvated K^+ ion would be expected to be larger than that of the solvated Cl^- ion in the mixtures. According to the Eyring theory of transport process in solution,[14] the activation energy corresponds to the energy required to provide a hole in the liquid for an ion to migrate and is anticipated to be larger for a larger ion. However, it is contrary to the prediction of the theory that the activation energy for the larger solvated ion K^+ is less than that for the smaller solvated ion Cl^-. This would suggest that the structure-breaking effect of the K^+ ion is greater than that of the Cl^- ion in the mixtures as well as in water.[15]

A small addition of ethanol to water enhances the structure of the solvent.[5] If the structure-breaking effect of the K^+ ion is greater than that of the Cl^- ion, the K^+ ion obtains the larger structural excess mobility than the Cl^- ion and the mobility of the K^+ ion becomes larger relative to the Cl^- ion in the mixtures. The intial increase in t_+ up to about 10 mol% of ethanol, where the slope of the viscosity of the mixtures plotted against the ethanol content shows a maximum,[16] would be primarily ascribed to the relative structure-breaking properties of these two ions. The concept mentioned above is readily applied to the temperature effect on transference numbers for KCl. Since the structure of the solvent is more enhanced at lower temperature, the difference in the structure-breaking effect between K^+ and Cl^- ions would become greater. Accordingly, the K^+ ion would obtain the larger structural excess mobility relative to the Cl^- ion and t_+ increases with decreasing temperature.

In addition to the structural effect, the sorting effect may be taken into consideration.[16] Since the viscosity of ethanol–water mixtures increases up to about 25 mol% of ethanol,[8,16] the effective viscosity around a solvated ion would become smaller than the bulk viscosity by selective enrichment of water molecules around a solvated ion, and the ion would have an excess mobility. This effect is larger for K^+ than for Cl^- ions since the crystallographic radius of a K^+ ion is smaller than that of a Cl^- ion. Hence the initial increase in t_+ would be also attributed to the difference in the sorting effect between these two ions. The sorting effect is expected to become greater at lower temperature since the sharper maximum of the bulk viscosity appears at lower temperature.[8,16]

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