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Effect of solvation with salting effect on solubilities of fluorocarbons in alcohols

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ABSTRACT

In our previous work, we found that salting-out effect of a fluorocarbon in an alcohol–NaOH solution brought solubility decrease which could be expressed in terms of the Setchenov coefficient. In this work, a group contribution method for the Setchenov coefficients was made, for dichrodifluoromethane (CFC-12), penafluoroethane (HFC-125), difluoromethane (HFC-32), 1,1,1,2-tetarfluoroethane (HFC-134a) and 1,1-difluoroethane (HFC-152a) in methanol–NaOH and ethanol–NaOH solvents. Moreover, as a simple model, we derived the relationship between the Setchenov coefficients and solvation number of alcohols around a NaOH molecule. Therefore, once information of the Setchenov coefficients was obtained, the solvation numbers could be predicted based on the model. Prediction of the Setchenov coefficients for VOC solublities in water–salt system is possible with the new method.

1. Introduction

Fluorocarbons containing chlorine atoms deplete the ozone layer, so that restrictions on production and transportation of chlorofluorocarbons (CFCs) were decided by the Montreal Protocol (1987) and hydrochlorinated fluorocarbons (HCFCs) are expected to be final in 2020. Massive wastes of CFCs and HCFCs will be treated in the near future which will be a serious problem.

We proposed a simple decomposition process of chlorinated fluorocarbons in alcohol containing NaOH at room temperature and atmospheric pressure with or without UV irradiation to produce other fluorocarbons, unsaturated compounds or fluoroethers with sodium chloride [1]. Especially, fluoroethers are expected to be the third generation refrigerants, because it decomposes rapidly in the air.

The dechlorination of the CFC or HCFC occurs after dissolving the gas in an alcohol–NaOH solution with or without UV irradiation. Being much slower than mass transfer rate, the reaction rate is governed by the solubility of fluorocarbons in alcohol–NaOH solutions. To design a reactor, solubility is the most important factor. To meet the requirement, we measured the Henry's law constants of fluorocarbons in alcohols at atmospheric pressure [2,3].

However, we found that solubility of a fluorocarbon in an alcohol–NaOH solvent decreased with NaOH concentration in a solution, i.e. salting-out effect. Reaction rate is proportional to both the concentration of the dissolved fluorocarbon and NaOH concentration in a solution [4]. The increase of NaOH brings the accelerator-brake effects that the one decreases due to salt-effect and the other increases. It is very interesting to know how concentration of NaOH affects the reaction rate. Therefore, we need the data on salting effects.

In a previous paper [5], we measured the solubilities of dichlorodifluoromethane (CFC-12, CCl_2F_2), pentafluoroethane (HFC-125, C_2HF_5), difluoroethane (HFC-152a, $C_2H_4F_2$), difluoromethane (HFC-32, CH_2F_2), 1,1,1,2-tetrafluoroethane (HFC-134a, $C_2H_2F_4$) in NaOH–methanol, NaOH–ethanol and NaOH-1-propanol solvents, ranging from 283 to 313 K at atmospheric pressure. As a result, the solubility of fluorocarbons decreases exponentially with the concentration of NaOH due to salting effects. This is known as the Setchenov relation and the Setchenov coefficients are typically independent of temperature.

In this work, we estimated the Setchenov (salting effect) coefficients in these systems with a group contribution method and the estimated values agreed very well with the experimental data. Moreover, according to a simple model, the Setchenov coefficient

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is related with solvation number of alcohols, and is expressed with a function of concentration of NaOH and partial pressure of fluorocarbon. Moreover, the group contribution method of the Setchenov coefficients were tried to apply this model to the water–VOC–salts systems.

2. Setchenov coefficient

The concentration of a fluorocarbon in an alcohol solution at temperature T, C_i^0 [mol/L] is expressed as the Henry's law equation:

$$C_i^0 = \frac{Py_i}{H_{ij}^0} \quad (1)$$

where P is the total pressure (= atmospheric pressure), y_i is the mole fraction of a fluorocarbon i in a vapor phase, superscript 0 means without NaOH and H_{ij}^0 is the Henry's law constant of a fluorocarbon i in an alcohol j solution without NaOH at temperature T [K].

When NaOH is added, the concentration of a fluorocarbon C_i [mol/L] in an alcohol–NaOH solution at experimental temperature T and at partial pressure Py_i is described as follows:

$$C_i = \frac{Py_i}{H_{ij}} \quad (2)$$

Since the addition of NaOH to an alcohol solvent has no effect on the partial pressure of fluorocarbon in the gas phase at the same experimental temperature and the same initial partial pressure [5], the following relationship is obtained from Eqs. (1) and (2),

$$\frac{C_i}{C_i^0} = \frac{H_{ij}^0}{H_{ij}} \quad (3)$$

Effects of electrolyte concentration on the solubilities of gases in solutions are known as salting-out or salting-in effects. The influence of the dissolved salt in the electrolyte solution is given by the Setchenov relation described as an exponential function of electrolyte concentration [6]. Although NaOH does not dissociate in alcohols, the effect of NaOH concentration on the solubility of 1,1,1,2-tetarfluoroethane (HFC-134a) in ethanol–NaOH at different temperatures is shown in Fig. 1. It shows that salting effect vary much less with temperature, however the solubilities of fluorocarbons decreased exponentially with NaOH concentration. Relation between solubility due to salting effect and C_{NaOH} is expressed as follows,

$$\frac{C_i}{C_i^0} = \exp(-h_{ij}C_{NaOH}) \quad (4)$$

where h_{ij} is the Setchenov coefficient (salting effect coefficient) of component i in alcohol j expressed in L/mol. It shows that the values of h_{ij} are proper for a system independent of temperature.

The Setchenov coefficients h_{ij} for the systems of dichlorodifluoromethane (CFC-12, CCl_2F_2), pentafluoroethane (HFC-125, C_2HF_5), difluoromethane (HFC-32, CH_2F_2), 1,1,1,2-tetrafluoroethane (HFC-134a, $C_2H_2F_4$) in methanol–NaOH, ethanol–NaOH solvents are listed in Table 1 in [5]. Table 1 shows the values of h_{ij} independent of temperature.

3. Estimation of Setchenov coefficient with group contribution method

We applied a group contribution method to the Setchenov coefficients obtained in the previous work [5]. The results show that contributions were divided into a solute (fluorocarbon) part and a solvent (alcohol) part. Four kinds of fluorocarbons, CH_2F_2 (CFC-12), C_2HF_5 (HFC-125), CH_2F_2 (HFC-32) and $C_2H_2F_4$ (HFC-134a), are composed of four elements of C—Cl, C—F, C—H and C—C. We assumed

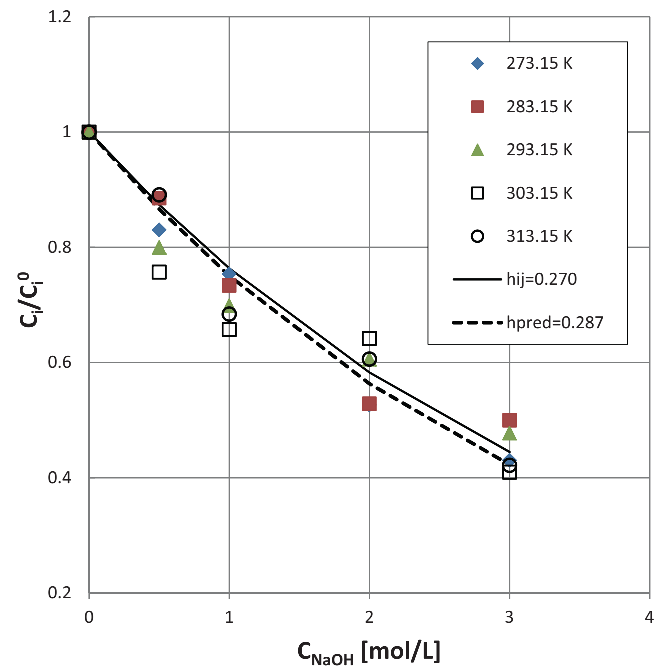

Fig. 1. Effect of NaOH concentration on solubility of HFC-134a in ethanol with changing temperature at atmospheric pressure of a solute gas ranging from 273.15 to 313.15 K: experimental [5].

that alcohols were characterized by bond numbers of C—H$_n$ (CH_2= or CH_3—) and C—C.

Contributions estimated by the least squares method are listed in Table 1. The Setchenov coefficients with the group contribution method are described as h_{pred}. The estimation h_{pred} agrees well with the experimental h_{ij} [5] as shown in Table 1. Comparison of solubilities of HFC-134a in ethanol–NaOH solvent using h_{pred} are shown also in Fig. 1. Differences between experimental values and predicted ones are very small. Table 1 enables to predict the Setchenov coefficients of fluorocarbons in methanol or ethanol. The results show that our method has predictability of fluorocarbons in methanol or ethanol. At present we have no other experimental data for the system. Further predictability will be considered in the future.

In the previous work [5], we found that addition of NaOH in higher alcohols produced gelatinization. For 1-propanol as a solvent, we could not estimate the precise values of h_{ij} with the group contribution method. In the higher alcohols, viscosity of a fluid must be considered.

4. Solvation

4.1. Solvation number of alcohol to NaOH molecule

Solubility of a fluorocarbon in an alcohol solvent without NaOH is expressed as,

$$S = \frac{C_i^0}{C_{alc}} \quad (5)$$

where superscript 0 means the concentration of a fluorocarbon without NaOH. Instead of j script alc is used for emphasis.

Salting-out effects can be explained as the solvation between salt (NaOH) and solvent (alcohol) and/or solute (fluorocarbon) as shown in Fig. 2.

Assuming fluorocarbons maintain vapor–liquid equilibrium with free alcohols excluding solvated alcohols, solubility of a solute