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Development of a group contribution method for determination of thermal conductivity of ionic liquids

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ABSTRACT

A group contribution (GC) method is proposed to estimate the thermal conductivity of ionic liquids covering a wide range of temperature (273.15–353.15 K) and thermal conductivity (0.1050–0.2137 W m^{-1} K^{-1}) based on experimental data collected from literature. A good agreement between the calculated and literature data was obtained for total 286 data points of 36 ionic liquids with an average absolute deviation (AAD) of 1.66%. The group contribution method developed in this paper offers a simple but reliable approach for estimating thermal conductivity for new ionic liquids in a wide temperature range at atmospheric pressure.

1. Introduction

Ionic liquids (ILs) have attracted much attention over the past decade due to their large varieties of applications in many chemistry and chemical industry fields [1]. Compared to numerous reports on the use of ILs in chemical reactions, there have been fewer investigations on their potential as heat-transfer fluids [2–6]. The desirable characteristics of a good heat-transfer fluid include a large liquidus range and good thermal stability. Some of the more common ILs (e.g., the dialkylimidazaolium salts) have exactly these characteristics. Thus, ILs have the potential to compete even with the most successful synthetic organic and silicone-based compounds in the heat-transfer fluid market [3]. For the rational design of ILs as heat-transfer fluids, it is important to investigate the thermophysical properties such as density, viscosity, and thermal conductivity. Compared to other thermophysical properties of ILs, only limited information on the thermal conductivity of ILs is available in the literature. Measurements and experiments on thermal conductivity are not always easy and cheap [7], therefore, it is of great importance to develop a method for estimating thermal conductivity of ionic liquids with a wide range of applicability and favorable accuracy.

Tomida et al. [8] proposed a correlation based on the Mohanty equation [9] to describe the relationship between the thermal conductivity and the viscosity of ILs,

$$\log\left(\frac{M_w\lambda}{\eta}\right) = 1.9596 - 0.004499M_w \quad (1)$$

where M_w is the molar mass, λ is the thermal conductivity, and η is the viscosity. Eq. (1) is obtained by assuming that the molar mass of the ILs is two times larger than the true value and it seems to work only for a limited number of anions [10]. As mentioned by the authors, Eq. (1) is not expected to give quantitative results.

Froba et al. [10] proposed another correlation based on the new thermal conductivity data for a series of 10 ILs at 293.15 K and atmospheric pressure,

$$\lambda\rho = A + \frac{B}{M_w} \quad (2)$$

where $A = 0.1130\,\mathrm{g\,cm^{-3}\,W\,m^{-1}\,K^{-1}}$ and $B = 22.65\,\mathrm{g^2\,cm^{-3}\,W\,m^{-1}\,K^{-1}\,mol^{-1}}$, and ρ is the density. We tried to extend this equation to other ILs and temperatures, however the results were not satisfactory with an average absolute deviation of 8.15%.

So far, there are only two predictive models available for the thermal conductivity of ILs[11]. One is the group contribution model proposed by Gardas and Coutinho [12], and the other is the perceptron neural network model proposed by Hezave et al. [7]. Both Gardas and Coutinho and Hezave et al.'s methods provide an average absolute deviation smaller than the experimental uncertainties (3–5%) [13,14] for the ILs in their papers, but also exist defects.

Gardas and Coutinho [12] suggested a simple linear correlation to describe the dependence of thermal conductivity on temperature,

$$\lambda = A_\lambda - B_\lambda T \quad (3)$$

where T is the absolute temperature, K, and A_λ and B_λ are fitting parameters that can be obtained from a group contribution

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approach. For 107 data points of 16 ILs the average deviation is 1.06%. However, their group division principle is lack of universality, for example, the anion is always defined as a group, thus, for new anions introduced to the data set, the group contribution values should be recalculated. Meanwhile, the lack of validation for different ionic liquid families limited the predictive capability of their method.

Most recently, Hezave et al. [7] proposed a model to estimate the thermal conductivity of pure ionic liquids based on artificial neural network (ANN). The thermal conductivity was considered as a function of molecular weight, melting point, temperature and pressure. The optimum number of hidden layers was determined to be one, with 13 neurons in the hidden layer and logarithmic-sigmoid and purelin functions as the transfer functions in the hidden and output layers, respectively. For 209 data points of 21 ILs the average deviation is 0.5%. However, to determine a thermal conductivity of ILs at a certain temperature and pressure, melting point T_m of ILs which is not always available and 79 parameters are needed.

Therefore, so far, we considered that the method proposed by Gardas and Coutinho was the best one to calculate thermal conductivity of ionic liquids with simple form and acceptable deviations.

In this work, a new method was presented for estimating thermal conductivity of ionic liquids based on the group contribution method, and this simple method allows the rapid and facile estimation of thermal conductivity with acceptable deviations for a wide range of ILs. A database of 286 data for 36 ionic liquids was covered.

2. Development of the method

The thermal conductivity of most liquids, including ionic liquids, decreases with temperature. Below or near the normal boiling point, the decrease is nearly linear. Over wide temperature ranges, Reidel[15] proposed a correlation to describe the variation of thermal conductivity (λ) with the absolute temperature (T),

$$\lambda = A\left[1 + \frac{20}{3}(1 - T_r)^{2/3}\right] \tag{4}$$

where $T_r = T/T_c$ is the reduced temperature, T_c is the critical temperature in K, A is a constant calculated from one single measurement.

Afterwards, a modified Reidel equation was proposed by Nagvekar[16] based on the second-order group contribution method,

$$\lambda = A'\left[1 + \frac{B'}{A'}(1 - T_r)^{2/3}\right] \tag{5}$$

where the constants A' and B' were estimated for some groups of organic compounds by the authors.

In this work, a new equation, which is similar in form to Reidel equation, was adopted to correlate the thermal conductivity of ionic liquids,

$$\lambda = \lambda_0\left[1 + k_0(1 - T_r)^{2/3}\right] \tag{6}$$

where k_0 is a temperature-independent constant, the critical temperature T_c is easy to obtained by Valderrama group contribution method[17] for several ionic liquids,

$$T_c = T_b/\left(\left[A + B\sum_{j=1}^{k} n_j \Delta T_c - \left(\sum_{j=1}^{k} n_j \Delta T_c\right)^2\right]\right) \tag{7}$$

where $A = 0.5703$ and $B = 1.0121$, n_j is the number of occurrences of a group j in the molecule, ΔT_c is the contribution to the critical temperature, and the boiling temperature T_b is calculated as,

$$T_b = 198.2 + \sum_{j=1}^{k} n_j \Delta T_b \tag{8}$$

where n_j is the number of occurrences of a group j in the molecule, and ΔT_b is the contribution to the boiling temperature. Their contributions to the boiling temperature T_b and the critical temperature T_c were determined in the same way that explained by Alvarez and Valderrama[18]. The consistency of Valderrama group contribution method has been checked using literature values of ionic liquid densities and compared with calculated values using a generalized correlation that makes use of those estimated critical properties[17]. This method is widely used in density estimation by Gardas et al. [19], high pressure phase behavior correlation by Carvalho et al. [20] and Alvarez et al. [21], heat capacity correlation by Ge et al. [22] and surface tension estimation by Wu et al. [23].

λ_0 is obtained by the group contribution method according to the following equation in this work,

$$\lambda_0 = \sum_{i=0}^{2} a_i \left(\sum_{j=1}^{k} n_j \Delta\lambda_{0,j}\right)^i \tag{9}$$

where n_j is the number of groups of type j, k is the total number of different groups in the molecule, and the parameters a_i and $\Delta\lambda_{0,j}$ were estimated as presented in Table 1 by minimizing the objective function O.F. in Eq. (10),

$$O.F. = \sum_{i=1}^{N_p} \left[\left|\lambda_{calc} - \lambda_{exp}\right| / \lambda_{exp}\right]_i \tag{10}$$

where N_p represents the number of data points. We selected 25 molecular groups to allow one to treat diverse types of ionic liquids. These groups are the same as used earlier by Joback and Reid [24], but with the inclusion of -CH_2 (with ammonium-, with phosphonium- and with others) [23].

Finally, we can obtain a new equation based on the group contribution method for thermal conductivity calculation,

$$\lambda = \sum_{i=0}^{2} a_i \left(\sum_{j=1}^{k} n_j \Delta\lambda_{0,j}\right)^i \left[1 + k_0(1 - T_r)^{2/3}\right] \tag{11}$$

286 data points for 36 ILs, based on imidazolium-, phosphonium-, and ammonium- cations with octylsulfate ($OcSO_4$), ethylsulfate ($EtSO_4$), bis(trifluoromethanesulfonyl) amide (NTf_2), hexafluorophosphate (PF_6), tetrafluoroborate (BF_4), chloride (Cl), trifluoromethanesulfonate (TfO), dicyanamide (DCA), tris(pentafluoroethyl)trifluorophosphate (FAP), acetate (CH_3COO), tricyanomethanide ($C(CN)_3$), serinate (Ser), taurinate (Tau), lysinate (Lys), threonate (Thr), prolinate (Pro), and valinate (Val) anion (see Supplementary material for more detail) were used in this work to obtain the values of the coefficients a_i and k_0 and the group parameters $\Delta\lambda_{0,j}$. The average absolute deviation (AAD) is defined as,

$$AAD(\%) = \frac{\sum_{i=1}^{N_p} \left|\left(\lambda_{calc} - \lambda_{exp}\right) / \lambda_{exp}\right|_i}{N_p} \tag{12}$$