Prediction of thermal conductivities for liquid mixture using ASOG-ThermConduct model

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Abstract

Thermal conductivity is one of transport properties relating to heat transfer required for designing chemical process. The authors have proposed the model for calculating liquid mixtures using excess thermal conductivity. The thermal conductivity for ternary system can be predicted using binary Wilson-TC parameters.

This paper deals with the prediction of thermal conductivity for liquid mixture using ASOG group contribution method. The group pair parameters for CH_2, ArCH, CyCH, H_2O, OH, CO and COO groups have been determined using the observed thermal conductivity data. The average deviations for binary systems discussed in this paper are 0.3 % and 2.1 % for non-aqueous and aqueous systems, respectively. The overall average deviations for 3 ternary systems is 1.25 %.

Keywords

Thermal conductivity, ASOG-ThermConduct model, group contribution method

1. Introduction

The thermal conductivities for liquid mixtures are one of important transport properties with kinematic viscosities and diffusion coefficients. Some correlative and predictive models have been proposed [1, 2]. The authors propose a correlative model of thermal conductivities using excess thermal conductivity [3].

This paper deals with proposal of ASOG-based model that gives the excess thermal conductivities using ASOG model [4-6]. Here the types between excess thermal conductivities and liquid composition are arranged. The systems discussed here are systems composed of CH_2, ArCH, CyCH, H_2O, OH, CO and COO groups. The system is 30 for solvent + solvent and solvent + water.

2. Calculation of liquid thermal conductivities using excess thermal conductivity model

The authors have proposed the following equation for calculation model of thermal conductivities for ideal liquid solution,

$$\ln \lambda M = \sum_i \ln\left(\lambda_i M_i\right) \qquad (1)$$

and the following equation for non-ideal solution mixture.

$$\ln \lambda M = \sum_i \ln\left(\lambda_i M_i\right) + \lambda^E \qquad (2)$$

Here v and M are thermal conductivity and molecular weight, respectively, and λ^E are excess thermal conductivity.

From the relationship [7] between the excess thermal conductivity and excess free energy,

$$\lambda^E = kG^E \qquad (3)$$

the following equation is used in this study.

$$\ln \lambda M = \sum_i \ln\left(\lambda_i M_i\right) - G^E / RT \qquad (4)$$

The authors have calculated the thermal conductivities at normal and high pressures using Wilson equation [8].

3. Calculation of thermal conductivity using ASOG method

3.1. Fundamental equation

The excess free energy has been given by the following ASOG-TC equation.

$$\ln \gamma_i = \ln \gamma_i^G \qquad (5)$$

$$\ln \gamma_i^G = \sum_k v_{k,i}\left(\ln \Gamma_k - \ln \Gamma_k^{(i)}\right) \qquad (6)$$

$$X_k = \sum_{i=1}^{n} x_i v_{k,i} \Big/ \left(\sum_l \sum_{j=1}^{n} x_j v_{l,j} \right) \qquad (7)$$

$$a_{k/l} = \exp\left(n_{k/l} / T\right) \quad (8)$$

Here, $n_{k/l}$ is ASOG-ThermConduct (ASOG-TC) parameter for thermal conductivity.

3.2. Determination of ASOG-TC parameters

Here, the group pair parameters for groups composed of CH2, ArCH, CyCH, H2O, OH, CO and COO groups have been determined using experimental thermal conductivity data. Table 1 shows the ASOG-TC parameters.

Table 1

ASOG-TC parameters

k	*l*	$n_{k/l}$	$n_{l/k}$
CH_2	ArCH	-0.88	-0.78
CH_2	CyCH	-9.27	5.69
CH_2	H_2O	-116.84	-108.10
CH_2	OH	1.46	2.36
CH_2	CO	-18.49	-3.90
CH_2	COO	0.00	0.00
ArCH	CyCH	-11.24	4.01
H_2O	OH	14.27	-6.96
OH	CO	-2.68	12.76
OH	COO	8.54	42.08
CO	COO	12.84	6.16

4. Calculation of thermal conductivities using ASOG-TC parameters

Table 2 shows the all evaluated results. The thermal conductivities for three binary systems, heptane + methyl cyclohexane, methyl cyclohexane + toluene, and 2-propanol + water that described in data collections by Stephan and Hildwein [9] have been evaluated using ASOG-TC parameters. The average deviations between the experimental and evaluated data are 0.10, 0.21 and 3.42 %. Figures 1 to 3 show the evaluated results for heptane + methyl cyclohexane, methyl cyclohexane + toluene and 2-propanol system (340 K).

Table 2

Evaluated results of thermal conductivities for binary systems

System		Temp.[K]	Dev. (%)	Ref.
(1)	(2)			
ethanol	heptane	253～293	0.40	10
heptane	toluene	253～283	0.27	10
heptane	methyl cyclohexane	340～370	0.11	9
heptane	acetone	253～293	0.58	10
acetone	ethanol	253～293	0.26	10
methyl cyclohexane	toluene	330～370	0.21	9
Ave. dev. (%)			0.30	
methanol	water	300～330	1.19	11
ethanol	water	300～330	1.69	11
2-propanol	water	320,340	3.42	9
Ave. dev (%)			2.10	
Total ave. dev. (%)			0.90	

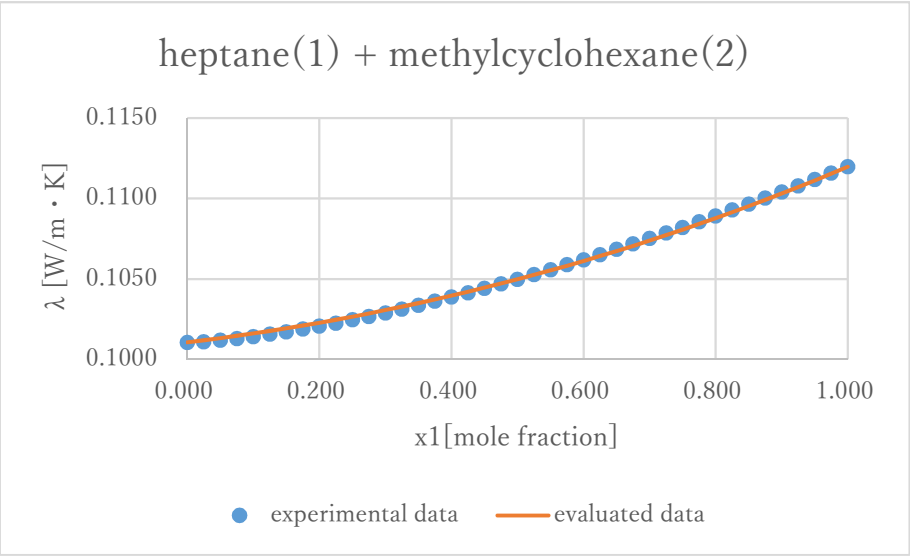

Fig.1. Thermal conductivities for heptane (1) + methyl cyclohexane (2) system (340 K)

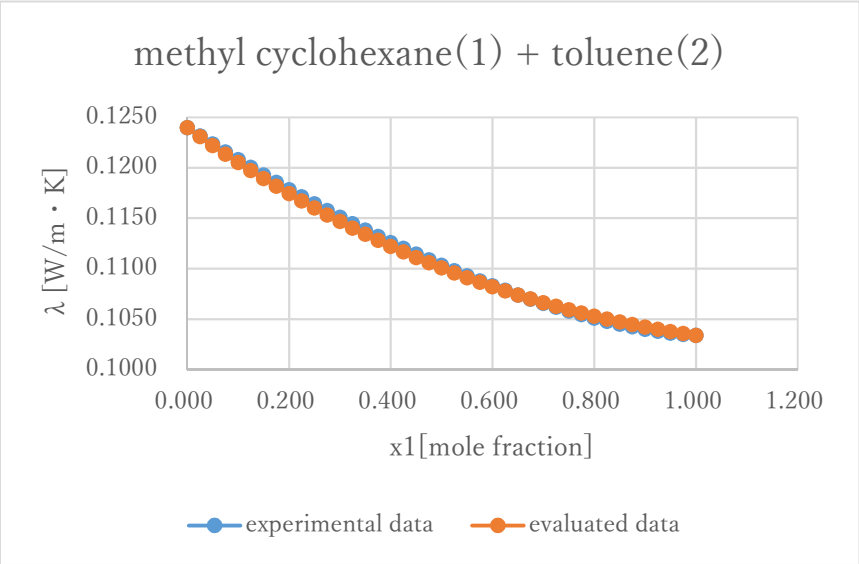

Fig. 2. Thermal conductivities for methyl cyclohexane (1) + toluene (2) system

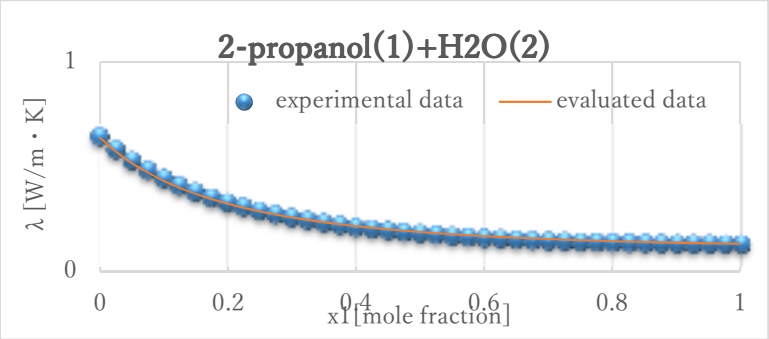

Fig. 3. Thermal conductivities for 2-propanol (1) + water (2) system (320 K)

Then, the thermal conductivities for 5 binary systems measured by Quin-Fang et al. [8] have been evaluated using ASOG-TC parameters. The overall average deviation is 0.12 %. Figures 4 to 6 show the evaluated results for ethanol + heptane, acetone + ethyl acetate and methanol + water systems.

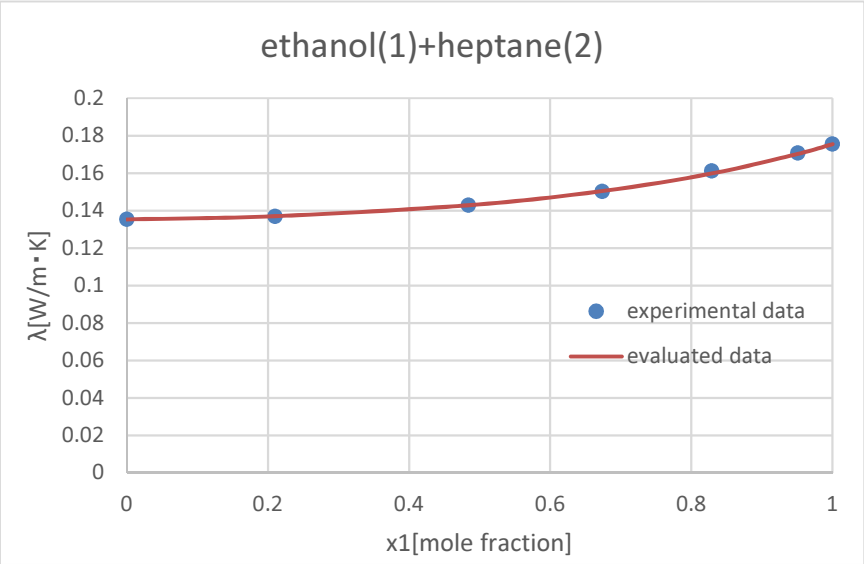

Fig. 4. Thermal conductivities for ethanol (1) + heptane (2) system (298.15 K)

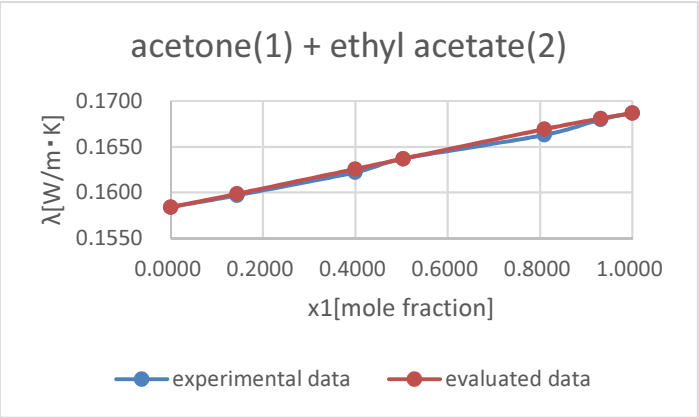

Fig. 5. Thermal conductivities for acetone (1) + ethyl acetate (2) system (298.15 K)

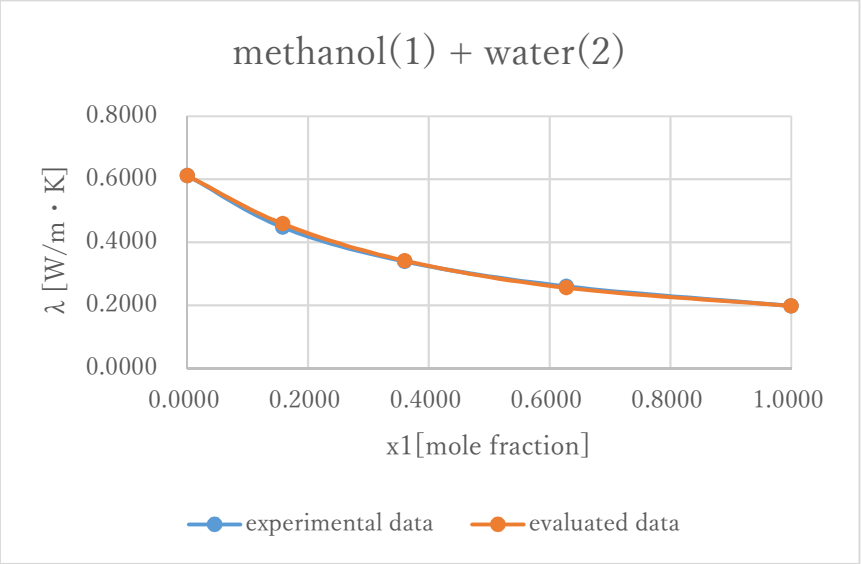

Fig. 6. Thermal conductivities for methanol (1) + water (2) system (300 K)

5. Conclusions

This paper deals with the prediction of thermal conductivity for liquid mixture using ASOG group contribution method. The group pair parameters for CH_2, ArCH, CyCH, H_2O, OH, CO and COO groups have been determined using the observed thermal conductivity data. The average deviations for binary systems discussed in this paper are 0.3 % and 2.1 % for non-aqueous and aqueous systems, respectively.

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