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Excess Enthalpies and Thermal Conductivity Coefficients for Binary Mixtures of Carbon Tetrachloride and Four Alkanes (C_5 to C_8) at a Temperature of 298.15 K

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Excess molar enthalpies have been measured for the binary mixtures of carbon tetrachloride, + pentane, + hexane, + heptane, and octane using a Paar 1455 solution calorimeter at a temperature of 298.15 K and atmospheric pressure. H^E values are positive over the entire range of compositions of carbon tetrachloride, and these data were used for calculation of NRTL model parameters (G_{12}, G_{21}). Finally, by using the local composition model, we calculated the thermal conductivity of these mixtures.

Introduction

The present work forms a part of our study on the thermodynamic properties of nonelectrolyte binary mixtures containing polar or nonpolar compounds.[1–3] This paper presents measurements on the excess enthalpies and calculates the thermal conductivity for the nonpolar systems carbon tetrachloride + normal alkanes pentane, hexane, heptane, and octane. The results can be applied for the development of heat transport study, the design of heat exchange equipment, and the study of thermodynamic behavior of some binary mixtures in which specific interactions between unlike molecules can occur. For calculating thermal conductivity, we applied the NRTL parameters G_{12} and G_{21} that were calculated based on excess enthalpy data and the local composition model for multicomponent liquid mixtures developed by Rowley.[4]

Experimental Section

Materials. The chemicals used in this study, their suppliers, and their purities are listed in Table 1. Carbon tetrachloride and normal alkanes were used without any further purifications. The purity of the components was checked by measuring their densities and refractive indices.

The densities were measured by using the Anton Paar-DMA 4500 density meter, and the refractive index was measured with an Abbé refracttometer. The uncertainty of the data is about ± 0.0001. Table 1 shows these experimental and literature values.[5]

Apparatus and Procedure. A Paar 1455 solution calorimeter was used for the measurement of excess enthalpies. The calorimeter consists of a dewar glass mixing chamber with a rotating sample cell, a thermistor probe, and a specially designed temperature bridge, all assembled in a compact cabinet. The temperature change can be plotted by using a computer program and can be read to an accuracy of ± 0.01 K. The two-piece cell serves as both the sample holder and agitation vessel, and it is closed with a detachable Teflon disk.

The liquid sample can be added to the cell from a pitot inserted through the top stem. Excellent thermal insulation is provided by the fully silvered dewar glass that serves as a mixing chamber. The enthalpy of mixing experiments were conducted in the calorimeter by considering 50 cm^3 of one component as solvent and a maximum of 25 cm^3 of the other component as solute. In the subsequent runs, 50 cm^3 of the previous solutions was taken as the solvent, and the pure solute was added to it. These experiments were continued until the concentration reaches (50 to 60) volume percent.

Table 1. Source, Purity Grades, Densities (ρ), and Refractive Indices (n_D) of the Pure Components

			ρ/g·cm^{-3} (25 °C)		n_D (25 °C)	
component	source	purity	exptl	lit.[5]	exptl	lit.[5]
octane	Merck	>99.0 %	0.7066	0.6985	1.3978	1.3951
heptane	Merck	>99.0 %	0.6839	0.6795	1.3885	1.3851
hexane	Merck	>99.0 %	0.6596	0.6548	1.3744	1.3723
pentane	Merck	>99.5 %	0.6226	0.6214	1.3587	1.3547
carbon tetrachloride	Merck	>99.8 %	1.5848	1.5844	1.4598	1.4574

This procedure was repeated by interchanging the components, and this method covers the entire concentration range. Initially, to determine the calorimeter equivalent, it was calibrated with 0.5 g of hydroxy methylaminomethane dissolved in 0.1 mol·dm^{-3} of hydrochloric acid solution that releases 254.52 J·g^{-1} at a temperature of 298.15 K.

The performance and reliability of the solution calorimeter was checked by making the measurement on a test mixture, cyclohexane + hexane, for which enthalpies of mixing were known.[6] Agreement between our data and that from the literature was better than 0.6 % over the central concentration of mole fraction of cyclohexane.

In the second part of this study, the parameters of the NRTL model (G_{12}, G_{21}) were calculated by using the experimental excess enthalpies and nonlinear Newton–Raphson method. Based on these calculated parameters and by using the local composition model for the multicomponent liquid mixture proved by Rowley,[4] we calculated the thermal conductivities for the systems where we measured their excess enthalpies.

Results and Discussion

The experimental results of excess enthalpies for the binary mixtures at a temperature of 298.15 K are given in Table 2 and shown in Figure 1. The results were fitted by the method of least-squares to the equation[7]

$$H^E(\text{J·mol}^{-1}) = x(1-x)\sum h_j(2x-1)^j \qquad (1)$$

where x represents the mole fraction of carbon tetrachloride, the values of the coefficients h_j, and the standard deviation $\delta(H^E)$

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Table 2. Excess Molar Enthalpies, H_m^E, and Thermal Conductivity Coefficients, k, for Binary Mixtures of Carbon Tetrachloride + Alkanes at Temperature of 298.15 K

x	H^E $J \cdot mol^{-1}$	k $W \cdot m^{-1} \cdot K^{-1}$	x	H^E $J \cdot mol^{-1}$	k $W \cdot m^{-1} \cdot K^{-1}$	x	H^E $J \cdot mol^{-1}$	k $W \cdot m^{-1} \cdot K^{-1}$
				(x) CCl_4 + $(1 - x)$ Pentane				
0.000	0.0	0.115	0.413	265.3	0.112	0.833	180.6	0.102
0.105	122.7	0.124	0.533	275.6	0.108	0.903	128.4	0.100
0.154	150.2	0.122	0.601	271.1	0.107	1.000	0.0	0.099
0.248	200.8	0.118	0.690	245.1	0.104			
0.306	225.3	0.115	0.750	225.3	0.103			
				(x) CCl_4 + $(1 - x)$ Hexane				
0.000	0.0	0.118	0.505	310.2	0.113	0.848	205.8	0.103
0.104	138.5	0.131	0.568	310.4	0.111	0.930	144.9	0.101
0.207	201.6	0.126	0.636	297.3	0.109	1.000	0.0	0.099
0.298	240.6	0.121	0.693	277.3	0.107			
0.394	285.6	0.117	0.764	242.1	0.105			
				(x) CCl_4 + $(1 - x)$ Heptane				
0.000	0.0	0.122	0.512	345.4	0.119	0.867	201.9	0.104
0.165	182.1	0.136	0.556	340.3	0.116	1.000	0.0	0.099
0.290	250.9	0.129	0.615	335.7	0.114			
0.388	311.6	0.124	0.696	310.4	0.110			
0.470	337.8	0.120	0.800	260.2	0.107			
				(x) CCl_4 + $(1 - x)$ Octane				
0.000	0.0	0.124	0.542	365.3	0.121	0.966	158.2	0.103
0.110	170.2	0.145	0.703	345.2	0.114	1.000	0.0	0.099
0.236	265.9	0.137	0.831	275.6	0.108			
0.414	350.7	0.127	0.920	210.4	0.105			

representing the fit of each set of results given in Table 3. The standard deviation has been calculated using the relation

$$\delta(H^E) = \left[\frac{\sum (H^E_{exptl} - H^E_{calcd})^2}{n - 1} \right]^{1/2} \qquad (2)$$

where n represents the number of data points.

The excess enthalpies are positive for all systems and showed maximum H^E values around (0.5 to 0.6) mol fraction of carbon tetrachloride. Since alkanes are strongly associated through hydrogen bonding, dilution with nonpolar solvents like carbon tetrachloride results in endothermic behavior. Excess enthalpies increased from pentane to octane with increasing chain length, which is from the effect of molecule site on the attraction force between them. It is observed that the excess enthalpies of all mixtures are relatively large despite the fact that all components are nonpolar. This may be attributed to the fact that the presence of four chlorine atoms in CCl_4 creates strong intermolecular interactions under the form of londonian forces, thus the mixing process with alkanes should be entirely assumed by the entropic contribution.

Table 3. Parameters h_j for Equation 1 and Standard Deviation δH^E for Different Binary Systems

	parameters					deviation
systems	h_0	h_1	h_2	h_3	h_4	$\delta(H^E)$ $J \cdot mol^{-1}$
CCl_4 + octane	1607.1	−183.2	2167.6	1247.7	5273.2	6.9
CCl_4 + heptane	1369.6	295.6	−213.7	−62.9	1095.1	5.7
CCl_4 + hexane	1256.6	106.7	−538.1	245.1	2007.4	4.3
CCl_4 + pentane	1108.8	135.7	−133.8	−64.1	881.8	3.7

Table 4. Parameters of the NRTL Model for Binary Systems Carbon Tetrachloride + Alkanes at a Temperature of 298.15 K

systems CCl_4 + alkanes	G_{12}	G_{12}	α_{12}
pentane	1218.3	54.1	0.2
hexane	1977.5	−360.2	0.2
heptane	2168.9	−398.1	0.2
octane	3747.2	−917.4	0.2

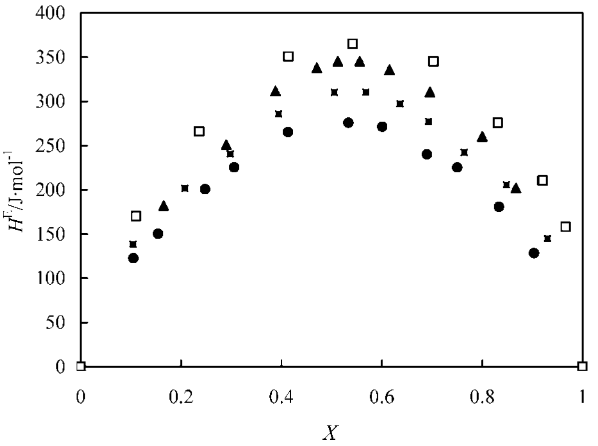

Figure 1. Excess molar enthalpy of carbon tetrachloride (x) + alkanes at a temperature of 298.15 K: ●, pentane; ×, hexane; ▲, heptane; □, octane.

Thermal conductivities of selected systems were calculated based on the equation[4]

$$k = \sum_{i=1}^{n} w_i \sum_{i=1}^{n} k_{ji} w_i G_{ji} \left(\sum_{i=1}^{n} w_i G_{ij} \right) \qquad (3)$$

G_{ij} and G_{ji} are the parameters of the NRTL equation that were calculated based on experimental excess enthalpy data and by using $\alpha = 0.2$; w_i is the mass fraction of component i; and $k_{ij} = k_{ji}$ are the characteristic parameters for thermal conductivity that express the interaction between i and j.[4]

Table 4 shows the NRTL parameters, and Table 2 and Figure 2 also show the calculated thermal conductivity for the selected systems at a temperature of 298.15 K based on eq 3. Mixtures of straight chain alkanes with carbon tetrachloride have similar behavior with respect to composition. Increasing chain length has a small increasing effect on the thermal conductivity, which is probably due to the fact that internal vibration modes of the molecules are important in thermal conduction as well as

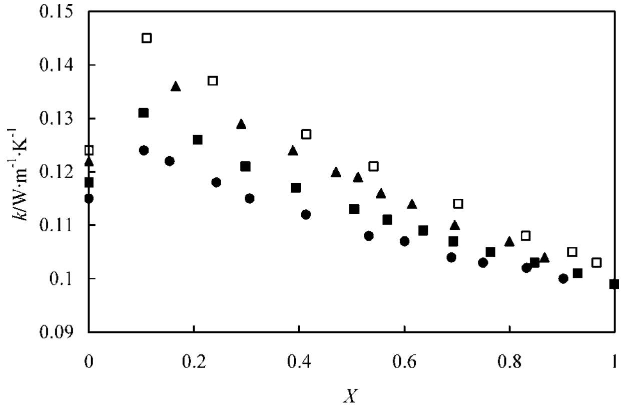

Figure 2. Thermal conductivities of carbon tetrachloride (x) + alkanes at a temperature of 298.15 K: ●, pentane; ■, hexane; ▲, heptane; □, octane.

translational modes. Comparison between some calculated thermal conductivity with the experimental values shows agreement especially at higher mole fractions (above 0.4) of carbon tetrachloride.[8,9] The method for prediction of mixture thermal conductivity presented here is based on a local composition model for the liquid, and at a lower mole fraction of carbon tetrachloride (below 0.4), the mixture behavior deviates from this model because of the difference between the structure of the solvent and solutes that affects the molecular interactions between components. Hydrogen bonding at a higher concentration of alkanes causes a deviation of the mixture from the local composition model. The NRTL model for thermal conductivity contains no adjustable parameters, yet it should be quite general because information concerning binary intermolecular interactions is input via equilibrium. This is an indirect and simple method for the calculation of the thermal conductivity coefficient of binary nonelectrolyte solutions by using excess enthalpy data from the literature.

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