Thermal Conductivity of Alcohols with Acetonitrile and *N,N*-Dimethylformamide

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The thermal conductivities of acetonitrile + 1,2-ethanediol, + methanol, + ethanol, + 1-propanol, + 1-butanol, + 1-pentanol, + 2-propanol, + 2-methylpropan-1-ol, + 3-methylbutan-1-ol, + 2-butanol, and *N,N*-dimethylformamide + 1,2-ethanediol, + methanol, + ethanol, + 1-propanol, + 1-butanol, + 1-pentanol, + 2-propanol, + 2-methylpropan-1-ol, + 3-methylbutan-1-ol, + 2-butanol were measured by the transient hot wire technique at 303.15 K with an estimated accuracy of better than ±0.8%. Five predictive equations were tested.

Introduction

The measurements on the thermal conductivity of pure liquids and mixtures are required for design problems involving heat transfer and the testing of theories and correlation and predictive models. There exist considerable thermal conductivity values of pure liquids and mixtures in the literature (*1–6*); further measurements are required to satisfactorily test correlations. A transient hot wire thermal conductivity apparatus was constructed, the thermal conductivities of twenty binary systems of alcohols with acetonitrile and *N,N*-dimethylformamide were measured at 303.15 K, and five predictive equations were tested.

Experimental Section

The transient hot wire technique is generally considered to be the most accurate method for the measurement of the thermal conductivity of fluids (*7–10*). When a thin wire immersed in a sample liquid is heated by an electrical current, the thermal conductivity of the sample can be determined from the temperature change of the wire and the energy added. If $\alpha t/a^2$ is large enough, the temperature rise ΔT is given by (*7*)

$$\Delta T = (q/4\pi\lambda) \ln(4\alpha t/a^2 C) \quad (1)$$

where λ is the thermal conductivity of the sample, q is the energy introduced per unit length of the wire, a is the radius of the wire, α is the thermal diffusivity, $C = \exp \gamma = 1.781$, γ is Euler's constant, and t is the time after the start of heating. Differentiating eq 1 with respect to ln t, the thermal conductivity of the sample can be calculated.

$$\lambda = (q/4\pi)/(\mathrm{d}\Delta T/\mathrm{d} \ln t) \quad (2)$$

According to the electrical circuit of the apparatus, eq 2 can be represented by the working equation (*7, 10*)

$$\lambda = (I^3/4\pi L)(\mathrm{d}R_w/\mathrm{d}T)(R_w S/(R_w + S))/(\mathrm{d}\Delta V/\mathrm{d} \ln t) \quad (3)$$

where I is the current through the platinum wire, L and R_w are the length and the resistance of the platinum wire between potential leads, S is the internal resistance of the bridge, $\mathrm{d}R_w/\mathrm{d}T$ is the temperature coefficient of the wire resistance, and ΔV is the transient voltage.

The apparatus is a modification of that described previously (*11*). Its schematic is shown in Figure 1, and the thermal conductivity cell is shown in Figure 2. The cell is designed for use to 10 MPa and 520 K. The platinum wire 25 μm in diameter and 100 mm in length is used as the heater with two potential leads spot-welded at a position 15 mm from the ends of the wire. The cell was immersed in a liquid thermostatic bath with a temperature stability of ±0.02 K. The temperature coefficient of the platinum wire was calibrated using a standard platinum thermometer.

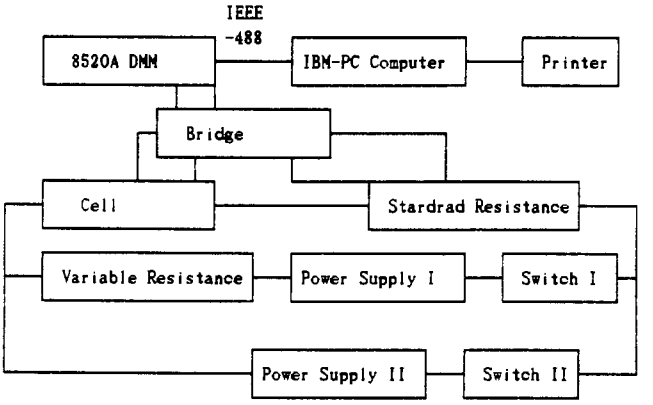

Figure 1. Block diagram for the instrumentation arrangement.

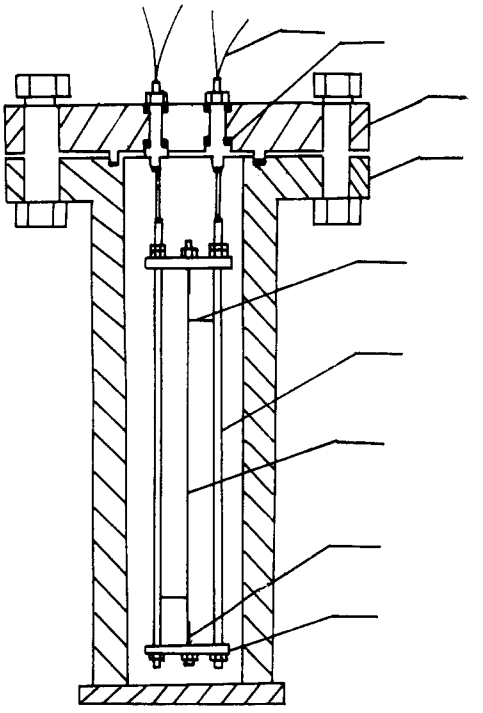

Figure 2. Structure of the thermal conductivity cell.

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The procedure for acquiring data was to initially balance the Wheatstone bridge. With switch I closed, a current of about 1 mA was passed through the bridge. The bridge balance was reached by correcting a small deviation in the null point, and the R_w was measured. About 20 min later, switch II was closed and an electric current of about 50 mA was passed through the wire to produce a significant heating of the wire. The change of the wire temperature in our experiments was about 1.5–2.5 K. The change of the wire resistance resulted in an out of balance voltage ΔV which was sampled at 20-ms intervals over 2500 ms by a Fluka 8520A digital multimeter connected to an IBM-PC computer via an IEEE-488 interface. The first 25 values were discarded because the finite heat capacity of the wire causes a noticeable error at short times (*2*). The thermal conductivity λ_1 at 0.9 s was obtained by the linear least-squares analysis of 20 measurements from ΔV_{26} to ΔV_{45}. In the same way, the values of λ_2, λ_3, λ_4, and λ_5 at 1.3, 1.7, 2.1, and 2.5 s were calculated from ΔV_{26} to ΔV_{65}, ΔV_{26} to ΔV_{85}, ΔV_{26} to ΔV_{105}, and ΔV_{26} to ΔV_{125}, respectively. The real thermal conductivity was obtained from a linear least-squares analysis of λ against time and extrapolation to zero time. For example, at 303.15 K λ_1, λ_2, ..., λ_5 for toluene are 129.6, 129.9, 130.1, 130.5, and 130.8 $mW \cdot m^{-1} \cdot K^{-1}$, respectively. The value at zero time by the extrapolation is 128.9 $mW \cdot m^{-1} \cdot K^{-1}$. This extrapolation corrects for radiation effects (*13*). Convection effects do not occur until 4 s into the experiment in our apparatus, so the results reported here are considered to be free of convection errors. The measurements were repeated from three to five times.

Estimation of Accuracy. The apparatus is designed so that the error due to departure from idealized conditions is small. The analysis has been described in detail elsewhere (*7, 11, 12*). The main uncertainties are estimated as follows (*7*): The uncertainty in measuring the length of the platinum wire between the potential leads is ±0.05%, that for the temperature coefficient dR_w/dT is ±0.1%, and that for the change of the introduced energy I^2R_w is ±0.2%. Two linear least-squares analyses give an uncertainty of ±0.2%. The total uncertainty is estimated at ±0.8%.

Source and Purity of Materials. All materials were analytical reagent grade purified by distillation in a 1.5-m-long column and dehydrated by standing over 3-Å molecular sieves. Gas liquid chromatography analysis indicated that the purities of all materials were better than 99.4%. Reagent grade 1,2-ethanediol was not distilled and had a purity determined by GLC as above of 99.0 mass %. All mixtures were prepared by mass with an accuracy of ±0.01%.

Results and Discussion

Thermal Conductivities of Pure Liquids. The thermal conductivities of 12 pure liquids measured at 303.15 K are listed in Table I. The thermal conductivity of toluene determined with our apparatus is 128.9 $mW \cdot K^{-1} \cdot m^{-1}$, close to the value of 129.5 $mW \cdot K^{-1} \cdot m^{-1}$ recommended by IUPAC (*14*). The other values are in reasonable agreement with the values reported in recent literature.

Thermal Conductivities of Binary Systems. The thermal conductivities of 20 binary mixtures at 303.15 K are given in Table II. All the binary mixtures show negative deviations compared with the ideal linear additive value λ_{id} (see predictive model). The thermal conductivities of the three systems acetonitrile + methanol, DMF + methanol, and DMF + ethanol exhibit a minimum.

Correlation of the Thermal Conductivities of Binary Mixtures. A number of predictive equations have been used. These include the Filippov equation (*15*), the Li equation (*15*), the power law (*15*), the Chen equation (*18*), and semiempirical models such as the local composition model (*17*) and the coordination model (*18*). The following five correlation equations were used to correlate the experimental results

Table I. Thermal Conductivities λ of Pure Liquids at 303.15 K and 0.1 MPa

substance	$\lambda/(mW \cdot K^{-1} \cdot m^{-1})$ this work	lit.	lit.	lit.
acetonitrile	201.2			
dimethylformamide	181.6	186.5 (*23*)	180.9 (*24*)	
1,2-ethanediol	253.1	253.5 (*21*)	252.7 (*22*)	
methanol	196.8	197.8 (*19*)	192.4 (*20*)	199.1 (*4*)
ethanol	162.6	160.7 (*19*)	166.5 (*20*)	159.8 (*5*)
1-propanol	151.2	149.2 (*19*)	151.6 (*20*)	149.2 (*5*)
1-butanol	145.4	147.0 (*19*)	146.4 (*4*)	145.6 (*5*)
1-pentanol	146.5	144.8 (*19*)	141.7 (*20*)	147.1 (*5*)
2-propanol	133.9	134.3 (*20*)	131.9 (*5*)	
2-methylpropan-1-ol	129.6	128.4 (*20*)	130.6 (*5*)	
3-methylbutan-1-ol	132.7	133.9 (*5*)		
2-butanol	133.5	133.4 (*20*)	134.0 (*4*)	133.0 (*5*)

1. additive mass fraction model

$$\lambda_{id} = w_1\lambda_1 + w_2\lambda_2$$

2. Filippov equation

$$\lambda = w_1\lambda_1 + w_2\lambda_2 - 0.72|\lambda_2 - \lambda_1|w_1w_2$$

3. Li equation

$$\lambda = \sum\sum \phi_i\phi_j\lambda_{ij}$$

$$\lambda_{ij} = 2(\lambda_i^{-1} + \lambda_j^{-1})^{-1}$$

$$\phi_i = x_iv_i/\sum x_iv_i$$

4. power law

$$\lambda = (w_1\lambda_1^{\,m} + w_2\lambda_2^{\,m})^m$$

$$m = 2 \quad \text{for} \quad 0 < \lambda_1/\lambda_2 < 1$$

5. Chen equation

$$\lambda = w_1\lambda_1 + w_2\lambda_2 - (c + |\lambda_1/\lambda_2 - 0.5|)w_1w_2(\lambda_2 - \lambda_1), \quad \lambda_2 > \lambda_1$$

$$c = (c_1 + c_2)/2$$

$$c_i = [b_{i1}(T_{ib} - T)/(T_{ib} - T_{im}) + b_{i2}]M_i/M_{i0}$$

where λ is the thermal conductivity, w is the mass fraction, x is the mole fraction, v is the molar volume, T_b is the boiling point, T_m is the freezing point, M is the molecular weight, and c, b, and M_0 are the parameters for pure liquid. For alcohol, $M_0 = 32.0$, $b_1 = 0.063$, and $b_2 = 0.025$ (*16*). For DMF $c = 0.45$ at 303.15 K. For acetonitrile $c = 0.23$ at 303.15 K.

The analysis is given in Table III. The overall average absolute deviations for the 20 binary systems from the additive mass fraction, Filippov, Li, power, and Chen equations are 2.3%, 1.71%, 1.34%, and 0.95%, respectively, which showed that the Chen equation is to be preferred for predictive purposes since it gives the least overall average deviation.

Table II. Thermal Conductivities λ of Acetonitrile + Alcohols and *N,N*-Dimethylformamide + Alcohols at 303.15 K at Mass Fraction w_2

w_2	λ/(mW·K^{-1}·m^{-1})	w_2	λ/(mW·K^{-1}·m^{-1})	w_2	λ/(mW·K^{-1}·m^{-1})	w_2	λ/(mW·K^{-1}·m^{-1})	w_2	λ/(mW·K^{-1}·m^{-1})	w_2	λ/(mW·K^{-1}·m^{-1})
Acetonitrile (1) + 1,2-Ethanediol (2)						*N,N*-Dimethylformamide (1) + 1,2-Ethanediol (2)					
0.0000	201.2	0.1000	206.3	0.8995	245.4	0.0000	181.6	0.0998	184.2	0.8995	240.2
0.4998	217.8	0.6995	229.5			0.4973	203.9	0.6979	219.7		
1.0000	253.1	0.3003	213.3			1.0000	253.1	0.3031	193.1		
Acetonitrile (1) + Methanol (2)						*N,N*-Dimethylformamide (1) + Methanol (2)					
0.0000	201.2	0.1000	198.4	0.8993	192.1	0.0000	181.6	0.0999	180.2	0.8997	190.3
0.4972	192.2	0.6987	191.9			0.4988	182.3	0.7000	184.9		
1.0000	196.8	0.3000	196.0			1.0000	196.8	0.3001	180.1		
Acetonitrile (1) + Ethanol (2)						*N,N*-Dimethylformamide (1) + Ethanol (2)					
0.0000	201.2	0.1005	196.6	0.8968	165.6	0.0000	181.6	0.1003	179.8	0.8987	161.8
0.5001	176.9	0.7001	171.0			0.4999	166.5	0.7001	164.6		
1.0000	162.6	0.3000	188.0			1.0000	162.6	0.3005	171.5		
Acetonitrile (1) + 1-Propanol (2)						*N,N*-Dimethylformamide (1) + 1-Propanol (2)					
0.0000	201.2	0.0997	198.4	0.9001	152.7	0.0000	181.6	0.1156	174.8	0.9001	153.9
0.5000	178.3	0.6089	162.2			0.4996	162.1	0.6996	155.9		
1.0000	151.2	0.3003	183.1			1.0000	151.2	0.3000	168.7		
Acetonitrile (1) + 1-Butanol (2)						*N,N*-Dimethylformamide (1) + 1-Butanol (2)					
0.0000	201.2	0.0996	197.7	0.8907	150.9	0.0000	181.6	0.1039	176.9	0.9000	147.9
0.4998	169.2	0.6992	158.1			0.4998	157.4	0.6982	153.0		
1.0000	145.4	0.2998	183.4			1.0000	145.4	0.3002	168.1		
Acetonitrile (1) + 1-Pentanol (2)						*N,N*-Dimethylformamide (1) + 1-Pentanol (2)					
0.0000	201.2	0.1005	196.2	0.9000	147.9	0.0000	181.6	0.1000	175.9	0.8995	150.0
0.50000	169.1	0.7000	156.8			0.5001	160.4	0.6999	152.0		
1.0000	146.5	0.3003	181.4			1.0000	146.5	0.3003	168.4		
Acetonitrile (1) + 2-Propanol (2)						*N,N*-Dimethylformamide (1) + 2-Propanol (2)					
0.0000	201.2	0.1211	191.8	0.8996	138.0	0.0000	181.6	0.1000	175.5	0.8987	136.9
0.5002	161.9	0.6941	149.6			0.4999	153.8	0.6984	143.4		
1.0000	133.9	0.3000	174.8			1.0000	133.9	0.2999	164.7		
Acetonitrile (1) + 2-Methylpropan-1-ol (2)						*N,N*-Dimethylformamide (1) + 2-Methylpropan-1-ol (2)					
0.0000	201.2	0.0997	193.4	0.8994	137.1	0.0000	181.6	0.1000	173.2	0.8991	134.3
0.5017	158.8	0.6978	146.4			0.5000	149.9	0.6989	141.2		
1.0000	129.6	0.3002	174.7			1.0000	129.6	0.3000	162.0		
Acetonitrile (1) + 3-Methylbutan-1-ol (2)						*N,N*-Dimethylformamide (1) + 3-Methylbutan-1-ol (2)					
0.0000	201.2	0.1000	192.2	0.8887	135.3	0.0000	181.6	0.1000	174.7	0.8843	137.0
0.4998	160.0	0.6990	147.9			0.5006	150.8	0.6998	140.8		
1.0000	132.7	0.3000	174.9			1.0000	132.7	0.3001	161.0		
Acetonitrile (1) + 2-Butanol (2)						*N,N*-Dimethylformamide (1) + 2-Butanol (2)					
0.0000	201.2	0.1038	188.4	0.9001	138.3	0.000	181.6	0.1029	175.0	0.8960	135.7
0.4994	161.1	0.6982	148.9			0.5001	154.2	0.6996	143.4		
1.0000	133.5	0.2996	174.2			1.0000	133.5	0.3013	161.3		

Table III. Summary of Average Deviations as ±100δλ/λ for Various Predictive Models

	model 1	model 2	model 3	model 4	model 5
acetonitrile + 1,2-ethanediol	2.07	0.82	0.82	0.97	1.02
acetonitrile + methanol	2.50	2.22	2.50	2.49	2.25
acetonitrile + ethanol	1.28	1.38	0.91	0.50	0.57
acetonitrile + 1-propanol	2.20	1.89	1.72	0.99	0.91
acetonitrile + 1-butanol	1.41	3.06	0.94	1.70	1.33
acetonitrile + 1-pentanol	2.30	1.90	1.75	1.28	0.99
acetonitrile + 2-propanol	2.55	2.66	1.14	1.77	0.39
acetonitrile + 2-methylpropan-1-ol	2.13	3.46	1.15	2.85	0.61
acetonitrile + 3-methylbutan-1-ol	3.23	2.10	1.93	1.74	0.62
acetonitrile + 2-butanol	3.09	2.33	1.84	1.35	0.64
average	2.28	2.18	1.47	1.56	0.93
N,N-dimethylformamide + 1,2-ethanediol	4.37	0.28	2.48	1.47	2.15
N,N-dimethylformamide + methanol	3.07	2.05	3.27	2.89	2.15
N,N-dimethylformamide + ethanol	1.96	0.84	1.60	1.71	0.98
N,N-dimethylformamide + 1-propanol	1.95	0.60	1.21	1.17	0.44
N,N-dimethylformamide + 1-butanol	1.76	1.03	0.74	0.59	0.66
N,N-dimethylformamide + 1-pentanol	1.64	1.05	0.88	0.69	0.76
N,N-dimethylformamide + 2-propanol	1.89	1.91	0.48	0.75	0.65
N,N-dimethylformamide + 2-methylpropan-1-ol	2.24	1.98	0.56	0.72	0.71
N,N-dimethylformamide + 3-methylbutan-1-ol	2.90	1.12	1.18	0.63	0.53
N,N-dimethylformamide + 2-butanol	2.39	1.49	0.82	0.67	0.63
average	2.41	1.23	1.32	1.13	0.97

The parameters for alcohol using the Chen equation were taken from the literature (*16*) while the parameters for acetonitrile and DMF were calculated in this work from the present results.

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