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Thermal Conductivity of Aqueous Mixtures of 2-*n*-Butoxyethanol at Pressures up to 150 MPa[†]

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This paper contains the results of new measurements of the thermal conductivity of mixtures of water and 2-*n*-butoxyethanol in the liquid phase within the temperature range of (304 to 346) K at pressures up to 150 MPa. The measurements were carried out with a transient hot-wire instrument and have an accuracy of ± 0.3 %. The investigation is the first conducted at high pressures on partially miscible mixtures whose components are of greatly differing thermal conductivity. It therefore provides a severe test of the methods of representing the thermal conductivity of liquid mixtures that are based on the hard-sphere theory of transport in liquids. It is shown that all of the experimental data may be represented to within ± 6 % by a "predictive" procedure based on the hard-sphere theory of liquids. However, a more detailed analysis of the results reveals small but systematic deviations from the universal behavior of the thermal conductivity as a function of molar volume that the predictive procedure and the hard-sphere theory have as their basis.

Introduction

There have been a number of significant advances in the measurement and prediction of the thermal conductivity of liquids and liquid mixtures.[1–6] However, for the most part these advances have been limited to hydrocarbons and their mixtures.[7–10] Further developments have made the experimental techniques[1,2,11,12] applicable to a range of polar and electrically conducting liquids. Such liquids generally have significantly different molecular interactions from those characteristic of hydrocarbons and undergo association and hydrogen bonding. Such mixtures often display regions of immiscibility for a range of thermodynamic states. Superficially, therefore, one would not expect such liquids, or mixtures of them, to conform to the results derived from the theory of hard-sphere of liquids which has proved so successful for hydrocarbons. The purpose of the present study is to provide accurate experimental data for the thermal conductivity of one such liquid mixture which can serve to test the applicability of the hard-sphere theory.

The system aqueous mixture of 2-*n*-butoxyethanol selected for study displays a lower critical solution temperature at 322.25 K for a mole fraction of 2-*n*-butoxyethanol of $x = 0.0478$ at a pressure of 0.1 MPa. It has therefore been the subject of a previous study to determine the behavior of the thermal conductivity in the neighborhood of the lower critical solution temperature.[2] This study revealed a small but significant enhancement of the thermal conductivity very close to the critical point. In the present work, we concentrate upon the region of states away from the critical, although we include numerical values of the results for the entire region studied.

Experiments

The measurements have been carried out in a transient hot-wire instrument described in detail elsewhere.[11,12] For the present work, the cells of the instrument were equipped with tantalum wires of 25 mm diameter in a fashion described earlier.[2] The entire wire assembly and its connecting wires are insulated in situ by means of an anodic layer of tantalum pentoxide as described elsewhere.[11] This arrangement serves to isolate the electrical components of the cell from the electrically conducting liquid. An automatic Wheatstone bridge described elsewhere is employed to obtain the time evolution of temperature of the tantalum wires during the application of a constant heat flux $q/\mathrm{W \cdot m^{-1}}$ to the transient hot-wire instrument. Due precautions were taken with the grounding of the cell to obviate dissolution of the anodic insulating layer while maintaining an appropriately low electrical noise level.[11]

The liquid mixtures were prepared gravimetrically from triply distilled water and 2-*n*-butoxyethanol supplied by Fluka Chemicals Ltd. with a purity in excess of 99.8 %. Four mixtures were prepared with mole fractions of 0.0478, 0.1732, 0.5000, and 0.7500. In each case the uncertainty in the mole fractions is less than ± 0.0001. The cells were filled by first evacuating them and subsequently introducing the liquid mixture under pressure by the method described earlier.[1] The working equations for the analysis of the experimental data have been given elsewhere,[3] and they are employed unchanged in this work.

The density and isobaric heat capacity values of the pure fluids and mixtures were required to make a number of small corrections during the analysis of the experimental data. For water, the density and heat capacity have been taken from the correlations of Haar et al.[13] For pure 2-*n*-butoxyethanol, the density and isobaric heat capacity were taken from the work of Malhotra and Woolf.[14] For the mixtures, Malhotra and Woolf have performed companion measurements of the density on

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Table 1. Thermal Conductivity of 2-*n*-Butoxyethanol

temperature, T (K)	pressure, P (MPa)	density, ρ_r ($kg\cdot m^{-3}$)	thermal conductivity $\lambda(T_{nom}, \rho_r)$ ($mW\cdot m^{-1}\cdot K^{-1}$)	thermal conductivity $\lambda(T_{nom}, P)$ ($mW\cdot m^{-1}\cdot K^{-1}$)
		T_{nom} = 304.15 K		
303.89	0.1	891.7	152.9	152.9
304.15	0.1	891.5	153.3	153.3
304.13	16.4	902.7	157.9	157.9
304.19	27.3	909.5	161.2	161.2
304.23	41.8	917.8	164.6	164.6
304.78	56.1	925.2	168.7	168.9
304.45	70.2	932.5	172.1	172.2
303.90	79.0	937.1	174.1	174.0
304.38	83.5	938.9	174.8	174.9
304.30	98.2	945.4	178.4	178.5
304.20	112.2	950.9	181.6	182.0
304.15	124.1	956.3	183.6	183.6
304.23	140.1	962.5	186.9	187.0
304.12	149.2	965.9	188.5	188.5
		T_{nom} = 321.15 K		
321.11	0.1	877.0	149.7	149.7
320.69	0.1	877.3	149.8	149.6
321.11	16.4	889.0	154.8	154.8
321.20	27.3	896.4	158.5	158.5
321.31	41.8	905.3	162.7	162.8
321.24	56.1	913.6	166.5	166.5
321.39	70.2	921.0	170.1	170.1
321.36	84.2	928.0	173.9	173.9
321.37	98.2	934.6	176.9	177.0
321.40	112.2	940.7	179.9	180.0
321.47	126.2	946.6	182.9	183.0
321.43	134.9	950.1	185.1	185.1
321.61	150.6	956.1	187.8	187.9
		T_{nom} = 338.15 K		
338.13	0.1	862.1	146.1	146.1
337.71	0.1	862.4	146.4	146.3
338.18	16.4	875.2	151.8	151.8
338.30	27.3	883.0	155.5	155.5
338.21	41.8	892.7	160.1	160.1
338.29	56.1	901.4	164.0	164.0
338.38	70.2	909.2	167.6	167.7
338.34	84.2	916.6	171.6	171.7
338.34	98.2	923.5	175.0	175.1
338.27	108.7	928.5	177.4	177.5
338.45	123.4	934.9	180.6	180.7
338.50	140.1	941.9	184.4	184.4

mixtures with the same compositions.[15] The isobaric heat capacity of the mixtures has been estimated as the mole-fraction average of the pure component values. The heat capacity influences a small correction in the analysis of the experimental data[3] which, in the present case, contributes no more than ± 1 % to the measured temperature rise. As a result, even quite large errors in the heat capacity have a negligible effect upon the reported thermal conductivity.

Results

Pure Components. Owing to the modifications to the transient hot-wire apparatus employed for the present measurements, it was appropriate to verify the correct operation of the instrument in accordance with the theory. This was particularly important for the present work on mixtures of water and 2-*n*-butoxyethanol because of the proximity of some of the thermodynamic states to the consolute point.[2] Table 1 lists the present results for the thermal conductivity of 2-*n*-butoxyethanol along three isotherms. The results for pure water along corresponding isotherms have been given in an earlier publication.[2] In each case, the experimental results have been corrected to nominal temperatures by application of small linear temperature corrections that never exceeded ± 0.2 %. It is estimated that the thermal conductivity listed has an accuracy of ± 0.5 % and a slightly better precision of ± 0.3 %.

For the purpose of comparison, the experimental data were represented by correlating equations of the form

$$\lambda(x, T, P) = \lambda'(x, T)\{1 + \sum_{i=0} b_i P_i^{*i}\} \tag{1}$$

where

$$P^* = (P - P')/P' \tag{2}$$

and P' is a normalizing pressure for each fluid, and x is the mole fraction of 2-*n*-butoxyethanol in the mixture. The values of the coefficients b_i and the normalizing pressure for both water and 2-*n*-butoxyethanol are included in Table 2. Figure 1 contains a comparison of the present results for 2-*n*-butoxyethanol with those of the correlating equation. The deviation plot has a maximum deviation of ± 0.3 % which is consistent with the estimated precision of the experimental results.

Mixtures. The experimental thermal conductivity data for the four mixtures studied along each of the four isotherms for mole fraction 0.0478 and along each of the three isotherms for mole fractions 0.1732, 0.5000, and 0.7500 are listed in

Table 2. Coefficients for the Representation of the Thermal Conductivity of 2-*n*-Butoxyethanol, Water, and Their Mixtures as a Function of Pressure According to Equation 1

x_1	T (K)	λ' ($mW\cdot m^{-1}\cdot K^{-1}$)	P' (MPa)	$10^2 b_1$	$10^2 b_2$	$10^2 b_3$	$10^2 b_4$
0.0	304.40	649.63	70	5.6375	−1.531	−1.435	1.2768
water	321.40	667.74	70	4.6589	1.9836	−0.100	−1.7044
	338.40	687.29	70	5.1571	0.0386	−0.748	−0.1363
0.0478	304.15	477.04	75	4.7138	−0.417	0.1672	0.2690
	317.15	485.62	75	5.0075	0.3115	0.0231	−0.4389
	320.90	489.86	75	5.3000	−1.621	−1.392	2.6743
	322.00	517.37	75	5.9830	−2.399	−1.047	2.3065
0.1732	313.15	301.99	75	6.7714	−0.942	−0.414	0.3808
	321.15	306.06	75	6.0626	−0.002	1.371	−1.043
	346.15	297.71	75	6.0154	−0.628	1.811	−2.016
0.5000	313.15	204.35	75	8.6463	0.7496	0.1574	−0.1991
	321.15	204.76	75	9.5020	−0.498	−0.107	−0.805
	344.15	202.92	75	9.0765	−1.473	1.014	0.1006
0.7500	313.15	185.79	75	9.428	−0.114	0.475	−0.932
	321.15	184.47	75	10.291	−1.347	0.270	−0.568
	344.15	182.35	75	11.006	−0.618	0.132	−0.807
1.000	304.15	173.20	75	10.250	−1.144	0.023	−0.230
2-*n*-butoxyethanol	321.15	171.47	75	10.886	−1.498	0.283	−0.100
	338.15	169.19	75	11.552	−1.605	0.349	−0.119

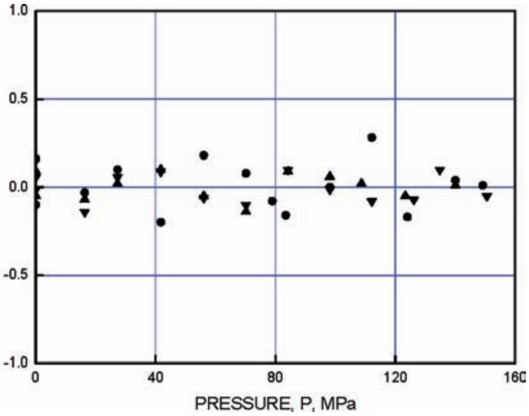

Figure 1. Deviations of the experimental thermal conductivity data of 2-*n*-butoxyethanol from their representation by means of eq 1 and the coefficients of Table 2. ●, 304.15 K; ▼, 321.15 K; ▲, 338.15 K.

Table 3. Thermal Conductivity of the 2-*n*-Butoxyethanol + Water Mixture [x(2-*n*-Butoxyethanol) = 0.0478]

temperature, T	pressure, P	density, ρ_r	thermal conductivity $\lambda(T_{nom}, \rho_r)$	thermal conductivity $\lambda(T_{nom}, P)$
(K)	(MPa)	($kg \cdot m^{-3}$)	($mW \cdot m^{-1} \cdot K^{-1}$)	($mW \cdot m^{-1} \cdot K^{-1}$)
		$T_{nom} = 304.15$ K		
303.37	0.1	979.2	453.7	453.3
303.78	14.2	985.5	457.0	456.8
303.77	27.3	991.4	462.4	462.2
303.84	41.8	997.6	468.2	468.0
303.90	55.4	1003.1	470.5	470.4
304.16	70.1	1008.8	475.8	475.8
305.06	83.9	1013.4	477.5	478.0
304.74	98.2	1019.0	484.2	484.5
304.33	112.1	1024.2	487.4	487.5
304.54	126.0	1028.9	491.5	491.7
304.26	138.7	1033.4	495.8	495.8
		$T_{nom} = 317.15$ K		
317.15	0.1	970.7	460.6	460.6
317.29	16.4	978.4	466.8	466.9
317.35	25.5	982.5	469.7	469.7
317.44	41.8	989.6	474.9	475.0
317.62	56.1	995.6	478.7	478.9
317.69	70.6	1001.4	484.8	485.0
317.71	84.2	1006.7	487.3	487.5
317.79	98.2	1011.9	492.4	492.6
317.68	112.2	1017.0	498.1	498.3
317.91	124.0	1021.0	500.5	500.8
317.87	141.0	1026.9	506.4	506.6
		$T_{nom} = 320.90$ K		
319.39	0.1	969.6	477.4	477.4
320.87	2.25	970.1	471.4	471.4
320.87	4.99	971.4	463.9	463.9
320.94	7.5	972.6	467.7	467.7
321.00	10.0	973.8	469.4	469.4
320.97	12.5	975.0	470.3	470.3
320.97	15.0	976.1	470.5	470.5
320.96	19.5	978.2	473.7	473.7
321.00	20.0	978.5	474.2	474.2
320.95	29.75	982.9	477.4	477.4
321.18	52.5	992.6	485.4	485.5
320.99	70.2	999.9	485.4	485.5
320.99	87.7	1006.7	498.6	498.6
320.97	105.2	1013.2	504.4	504.4
321.06	126.2	1020.7	512.3	512.3
		$T_{nom} = 322.00$ K		
321.94	0.1	968.6	493.2	493.2
321.93	5.41	971.2	488.6	488.6
321.52	20.0	978.3	493.3	493.1
322.07	34.6	984.6	500.6	500.6
322.12	52.5	992.3	506.9	506.9
321.94	70.2	999.6	514.9	514.9
321.91	87.7	1006.4	522.2	522.1
321.69	105.2	1013.0	528.2	528.0
321.87	119.2	1018.0	532.3	532.2
321.77	133.2	1022.9	535.6	535.4

Tables 3 to 6. The data have again been corrected to nominal temperatures by application of small linear temperature corrections, and the results have an estimated accuracy of ± 0.5 %. Correlation equations similar to that in eq 1 for the pure liquids have been employed to represent the experimental thermal conductivity data as a function of pressure for each isotherm and for each mixture, and the appropriate coefficients are listed Table 2.

Figures 2 to 5 display the deviations of the experimental data from the optimum representation by the correlation eq 1 for the four mixtures. The maximum deviation from the correlation occurs for the mixture with a 2-*n*-butoxyethanol mole fraction of 0.0478 at a temperature very close to the consolute temperature for atmospheric pressure where it reaches 1.5 %. This behavior reflects that of the thermal conductivity near the consolute point discussed elsewhere.[2] More generally, the maximum deviation of the experimental data for the correlation is ± 0.5 %, while the standard deviation of the whole data set is ± 0.2 %.

Density Dependence of the Thermal Conductivity. Assael, Dymond, and their collaborators in a series of papers[16–21] have investigated the manner in which the model of a hard-sphere fluid can be used as a basis of procedure to represent the experimental data for the transport properties of polyatomic liquids and their mixtures.

The systems considered in their investigations included normal alkanes and their mixtures as well as pure aromatic hydrocarbons and organic and inorganic molecules. The present system has not previously been considered in any of these analyses since it is an aqueous mixture. Given the success of the proposed scheme of Dymond et al.,[16–20] it is worthwhile to examine the extent to which the present system can be represented by the established scheme. In addition, because of the importance in the system of attractive interactions and the existence of a consolute point, it provides an extreme test of any procedure for the representation of its thermal conductivity by a method based upon the hard-sphere theory of fluids.

For the purpose of establishing the extent to which the present system conforms to the scheme of Dymond et al.[16–20] and Assael et al.,[21] we employ a reduced thermal conductivity, λ^*, which is given in terms of experimental quantities as

$$\lambda^*_{exp} = 1.936 \cdot 10^7 R_\lambda \left[\frac{M}{RT}\right]^{1/2} \lambda_{exp} V^{2/3} \qquad (3)$$

Here, λ_{exp} is the measured thermal conductivity of the fluid or fluid mixtures with a molar mass M at a temperature T and a molar volume V.

It is a result of the modifications of the rough hard-sphere theory of dense fluids[16–20] that

$$\lambda^* = R_\lambda \lambda^* \left(\frac{V}{V_o}\right)$$

wherein R_λ is a roughness factor for the thermal conductivity which is temperature and density independent, while $\lambda^*(V/V_o)$ is a function only of the ratio of the molar volume, V, to the characteristic molar volume V_o, which, for a given system, depends only on temperature. Values of R_λ and $V_o(T)$ for each system can be defined once a reference function $\lambda^*(V/V_o)$ has been defined.

Table 4. Thermal Conductivity of the 2-*n*-Butoxyethanol + Water Mixture [x(2-*n*-Butoxyethanol) = 0.1732]

			thermal conductivity	
temperature, T	pressure, P	density, ρ_r	$\lambda(T_{nom}, \rho_r)$	$\lambda(T_{nom}, P)$
(K)	(MPa)	($kg \cdot m^{-3}$)	($mW \cdot m^{-1} \cdot K^{-1}$)	($mW \cdot m^{-1} \cdot K^{-1}$)
T_{nom} = 304.15 K				
303.86	0.1	938.2	281.4	281.3
304.17	20.3	948.5	285.7	285.7
304.20	30.0	953.2	289.6	289.6
304.17	47.2	961.2	294.2	294.2
304.23	70.2	971.0	300.7	300.8
304.24	84.2	976.7	304.3	304.3
304.44	98.2	981.9	307.6	307.7
303.39	110.4	986.5	310.9	311.0
304.43	126.2	992.1	314.5	314.7
304.49	140.1	996.8	317.3	317.5
304.54	150.6	1000.3	319.4	319.5
T_{nom} = 335.00 K				
334.90	0.1	911.9	280.5	280.4
334.92	10.0	917.8	285.1	285.1
335.08	19.0	922.8	289.4	289.5
335.50	41.8	934.5	297.0	297.2
334.98	70.2	948.3	306.0	306.0
335.10	84.2	954.4	307.7	307.7
335.12	98.2	960.2	311.1	311.1
334.86	112.2	965.9	315.4	315.3
334.91	125.5	970.9	320.5	320.5
335.18	137.3	975.1	321.8	321.8
T_{nom} = 346.50 K				
346.89	0.1	901.1	265.5	265.9
346.57	10.0	907.6	275.2	275.3
346.47	20.0	913.6	279.6	279.6
346.59	29.5	918.8	283.4	283.4
346.58	49.0	929.1	290.4	290.4
346.40	84.2	945.7	301.0	300.9
346.47	98.2	951.7	302.9	302.9
346.41	112.2	957.4	304.6	304.6
346.59	122.7	961.4	309.9	310.0
346.74	140.1	967.9	312.2	312.2
346.59	148.5	971.0	312.8	312.8

Table 5. Thermal Conductivity of the 2-*n*-Butoxyethanol + Water Mixture [x(2-*n*-Butoxyethanol) = 0.5000]

			thermal conductivity	
temperature, T	pressure, P	density, ρ_r	$\lambda(T_{nom}, \rho_r)$	$\lambda(T_{nom}, P)$
(K)	(MPa)	($kg \cdot m^{-3}$)	($mW \cdot m^{-1} \cdot K^{-1}$)	($mW \cdot m^{-1} \cdot K^{-1}$)
T_{nom} = 304.15 K				
304.63	0.1	909.3	183.7	183.7
304.65	10.3	915.7	187.4	187.7
304.60	15.0	918.5	188.9	189.0
304.56	26.7	925.2	193.5	193.6
304.49	41.8	933.2	196.2	196.3
304.50	54.7	939.6	199.4	199.5
304.44	70.2	946.8	203.1	203.2
304.44	84.2	953.0	206.5	206.6
304.47	108.7	962.9	212.6	212.7
304.40	124.8	969.1	215.6	215.7
304.40	140.1	974.6	218.8	218.9
T_{nom} = 321.15 K				
320.64	0.1	894.7	183.1	182.9
320.63	10.0	901.5	186.6	186.4
320.84	19.3	907.0	189.3	189.2
320.66	19.7	907.4	189.8	189.6
320.84	41.8	919.9	196.0	195.9
320.83	56.1	927.4	200.2	200.1
320.80	70.2	934.3	203.5	203.4
320.83	84.2	940.7	207.5	207.3
320.77	96.5	946.1	210.0	209.9
320.87	112.2	952.5	214.5	214.4
320.90	126.9	958.3	217.3	217.2
320.93	141.5	963.7	220.2	220.1
320.94	149.9	966.7	221.4	221.3
T_{nom} = 338.15 K				
338.44	0.1	877.9	179.5	179.6
338.28	10.4	885.6	184.0	184.1
338.50	19.5	891.6	186.6	186.7
338.40	19.0	891.4	186.5	186.6
338.48	41.8	905.4	193.5	193.6
338.42	56.1	913.4	198.5	198.6
338.66	70.2	920.5	201.6	201.8
338.75	80.7	925.6	203.7	203.9
338.75	98.2	933.7	208.1	208.3
338.73	112.2	939.8	211.6	211.8
338.80	126.2	945.5	214.4	214.6
338.73	140.8	951.2	218.1	218.3

Prediction Scheme. To examine the ability of the general scheme of Dymond, Assael, and their collaborators[16–21] to predict the present experimental data, we have employed their proposed universal representation of λ^* as a reference function. It is given by

$$\log(\lambda^*_{exp}/R_\lambda) = \sum_{i=0}^{4} a_{\lambda_i}\left(\frac{1}{V_r}\right)^i \tag{4}$$

where

$$V_r = V/V_o^u \tag{5}$$

and the superscript u indicates the use of the universal function of eq 5 in the definition of V_o. The coefficients $a_{\lambda i}$ are given in the work of Assael et al.[16–21] For the two pure fluids studied here, the values of R_λ and V_o have been determined by means of the superimposition of the experimental values of λ^* for the pure liquids at each temperature upon the universal function given by eq 4. For the mixtures, the values of R_λ and V_o were evaluated according to the procedures proposed by Assael et al.[17] in an earlier investigation and reaffirmed subsequently in a recent publication,[21] namely

$$V_o(x_1, T) = V_{o_1}x_1 + (1 - x_1)V_{o_2} \tag{6}$$

and

$$R_\lambda(x_1) = x_1R_{\lambda_1} + (1 - x_1)R_{\lambda_2} \tag{7}$$

while for the molar mass we employ the relation

$$M = x_1M_1 + (1 - x_1)M_2 \tag{8}$$

In this case, x_1 denotes the mole fraction of 2-*n*-butoxyethanol, which is distinguished throughout by subscript 1, while the subscript 2 denotes water. Table 7 lists the values of R_λ and V_o determined by this procedure. It should be noted that whereas these procedures are representational in the case of the pure fluids they are *predictive* in the case of the mixtures.

Figure 6 contains a plot of the deviations of the present experimental data from those predicted from the procedure of Dymond, Assael, and their collaborations[16–20] using eqs 4 to 8. The results are consistent with the claims of Assael et al.[16–20] that their procedure has an accuracy of ± 6 % for the estimation of the thermal conductivity of the liquid mixtures. It follows that their procedure can be used to predict the thermal conductivity of water and 2-*n*-butoxyethanol and their mixtures over a wider range of thermodynamic states than have been covered in the measurements here with the same level of confidence.

Table 6. Thermal Conductivity of the 2-*n*-Butoxyethanol + Water Mixture [*x*(2-*n*-Butoxyethanol) = 0.7500]

			thermal conductivity	
temperature, T	pressure, P	density, ρ_r	$\lambda(T_{nom}, \rho_r)$	$\lambda(T_{nom}, P)$
(K)	(MPa)	($kg \cdot m^{-3}$)	($mW \cdot m^{-1} \cdot K^{-1}$)	($mW \cdot m^{-1} \cdot K^{-1}$)
		T_{nom} = 304.15 K		
304.24	0.1	898.6	165.5	165.5
304.19	10.3	905.4	169.0	169.0
304.19	19.3	911.0	171.7	171.7
304.14	39.5	922.6	177.1	177.1
304.20	54.7	930.5	181.2	181.2
304.21	76.5	941.0	186.2	186.2
304.28	91.2	947.5	190.0	190.0
304.42	98.2	950.4	190.0	190.1
304.36	112.2	956.2	195.0	195.1
304.37	127.6	962.2	197.5	197.6
304.36	140.1	966.8	200.4	200.5
304.37	150.6	970.6	202.1	202.2
		T_{nom} = 321.15 K		
320.96	0.1	883.5	162.4	162.4
320.98	10.0	890.6	165.6	165.6
320.96	19.3	896.9	169.3	169.3
320.94	28.3	902.7	171.8	171.8
320.92	39.3	909.3	174.5	174.4
320.89	56.1	918.6	179.3	179.2
320.87	71.6	926.6	183.7	183.6
320.84	84.2	932.7	187.2	187.1
320.80	98.9	939.4	190.8	190.7
320.78	111.5	944.8	193.0	192.9
320.81	124.8	950.3	196.0	195.9
320.82	142.2	957.0	199.9	199.8
320.83	150.6	960.2	201.7	201.6
		T_{nom} = 338.15 K		
338.89	0.1	867.0	159.1	159.4
338.17	11.0	876.2	163.7	163.7
338.30	19.5	882.3	166.3	166.3
338.25	30.7	889.9	170.2	170.2
338.18	39.3	895.5	172.3	172.3
338.17	56.1	905.4	176.7	176.7
338.17	70.2	913.1	181.2	181.2
338.14	91.2	923.6	186.8	186.8
338.06	105.2	930.2	190.7	190.7
338.20	117.8	935.6	192.4	192.4
338.04	131.8	941.6	196.4	196.4
338.05	147.1	947.6	199.7	199.7

Although the predictive scheme of Assael et al.[16–20] is evidently quite successful in describing the thermal conductivity of the present system, it is equally possible to discern in Figure 6 that there are systematic deviations of the experimental data from the predictive scheme. The deviations arise from the density dependencies of the reduced thermal conductivity of the mixtures which are significantly different from that of the universal function of Assael et al.[16–20]

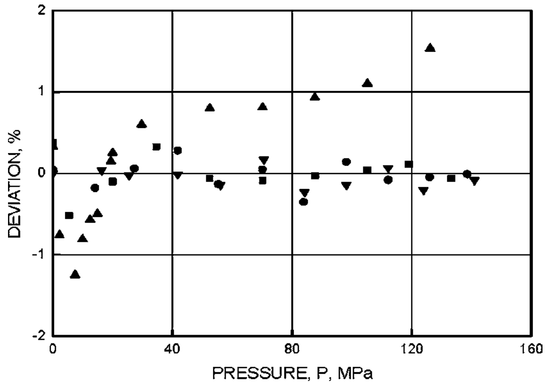

Figure 2. Deviations of the experimental thermal conductivity data of a mixture of 2-*n*-butoxyethanol and water *x*(2-*n*-butoxyethanol) = 0.0478 from their representation by means of eq 1 and the coefficients of Table 2. ●, 304.15 K; ▼, 317.15 K; ▲, 320.90 K; ■, 322.00 K.

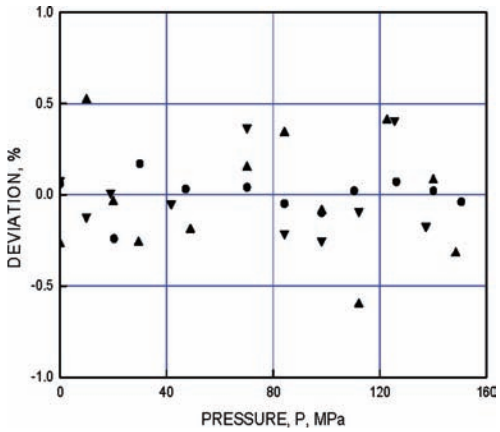

Figure 3. Deviations of the experimental thermal conductivity data of a mixture of 2-*n*-butoxyethanol and water *x*(2-*n*-butoxyethanol) = 0.1732 from their representation by means of eq 1 and the coefficients of Table 2. ●, 304.15 K; ▼, 335.15 K; ▲, 346.15 K.

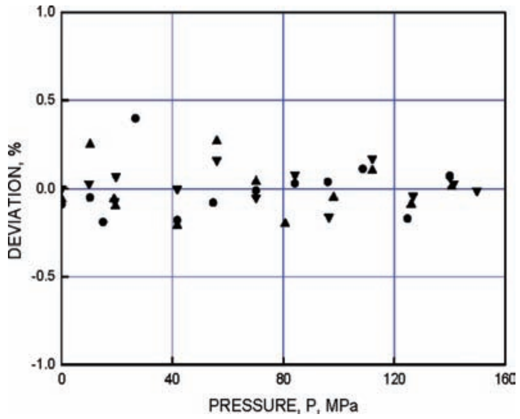

Figure 4. Deviations of the experimental thermal conductivity data of a mixture of 2-*n*-butoxyethanol and water *x*(2-*n*-butoxyethanol) = 0.5000 from their representation by means of eq 1 and the coefficients of Table 2. ●, 304.15 K; ▼, 321.15 K; ▲, 338.15 K.

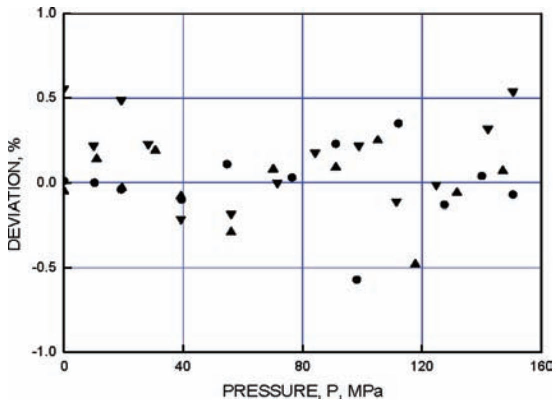

Figure 5. Deviations of the experimental thermal conductivity data of a mixture of 2-*n*-butoxyethanol and water *x*(2-*n*-butoxyethanol) = 0.7500 from their representation by means of eq 1 and the coefficients of Table 2. ●, 304.15 K; ▼, 321.15 K; ▲, 338.15 K.

Furthermore, the density dependencies of the reduced thermal conductivity of the pure liquids and their mixtures differ considerably among themselves so that the representation of the behavior of the thermal conductivity of the system with a single function $\lambda^*(V/V_o)$ is not possible. This indicates that, at a level consistent with the precision of the present

Table 7. Values of Roughness Factor, R_λ, and Characteristic Volume, V_o^u, for Use with the "Universal" Correlation of Equation 4

mole fraction 2-*n*-butoxyethanol	R_λ	temperature, T (K)	V_o ($10^{-6}\cdot m^3\cdot mol^{-1}$)
0.0 water	1.005	304.40	12.365
		321.4	12.395
		338.15	12.425
0.0478	1.0935	304.15	15.844
		317.15	15.868
		320.90	15.875
		322.00	15.877
0.1732	1.325	313.15	24.928
		321.15	24.954
		346.15	24.999
0.5000	1.930	313.15	48.631
		321.15	48.651
		344.15	48.723
0.7500	2.393	313.15	66.764
		321.15	66.779
		344.15	66.871
1.000 2-*n*-butoxyethanol	2.855	304.15	84.900
		321.15	84.907
		338.15	85.020

Table 8. Values of Characteristic Volume, V_o, and Coefficients of Equation 9

mole fraction 2-*n*-butoxyethanol	temperature, T (K)	V_o ($10^{-6}\cdot m^3\cdot mol^{-1}$)	coefficients of eq 9 c_o	 c_1	 c_2
0.0 water	304.40	12.365	322.132	−669.11	404.53
	321.40	12.395			
	338.15	12.425			
0.0478	304.15	15.844	304.294	−693.65	390.79
	317.15	15.868			
	320.90	15.875	107.405	−81.794	−1.872
	322.00	15.877	−156.147	697.49	−572.97
0.1732	313.15	24.928	165.727	−280.56	159.11
	321.15	24.954			
	346.15	24.999			
0.5000	313.15	48.631	159.483	−290.87	192.226
	321.15	48.651			
	344.15	48.723			
0.7500	313.15	66.764	169.391	−297.57	200.143
	321.15	66.779			
	344.15	66.871			
1.000 2-*n*-butoxyethanol	304.15	84.900	89.830	−93.583	53.122
	321.15	84.907			
	338.15	85.020			

experimental data, the density dependence of the thermal conductivity of the 2-*n*-butoxyethanol + water system is not universal. Therefore, we examine the behavior of the system in more detail to seek an improved representation of the experimental results.

Improved Representation. To secure an improved representation of the thermal conductivity, we retain the idea that, for a particular fluid, the temperature dependence of the reduced thermal conductivity, λ^*, is contained exclusively within the core volume V_o. However, we discard the idea that the density dependence of λ^* is universal among different fluids. Thus, we seek to represent the density dependence of λ^* for the two pure fluids and each of their mixtures independently by means of an equation of the form

$$\left(\frac{\lambda^*}{R_\lambda}\right)\left({}^{V}/_{V_o}\right)^{7/3} = \sum_{i=0}^{2} c_i\left({}^{V}/_{V_o}\right)^{i} \qquad (9)$$

where, now, both R_λ and the values of c_i depend upon the pure fluid or the mixture composition. Here, the factor $(V/V_o)^{7/3}$ on the left-hand side is chosen to remove the dominant contribution to the density dependence of λ^*. In performing this analysis, the values of R_λ and V_o listed in Table 8 were employed. The values of V_o for each temperature for each of the mixtures were determined by the condition that for each mixture they should be those yielding optimum superposition according to eq 9 using the value for the lowest isotherm as the reference. The values of R_λ remain those of Table 7, while values of V_o together with the coefficients c_i of eq 9 that secure the optimum representation of the entire set of data for each pure component and mixture are listed in Table 8.

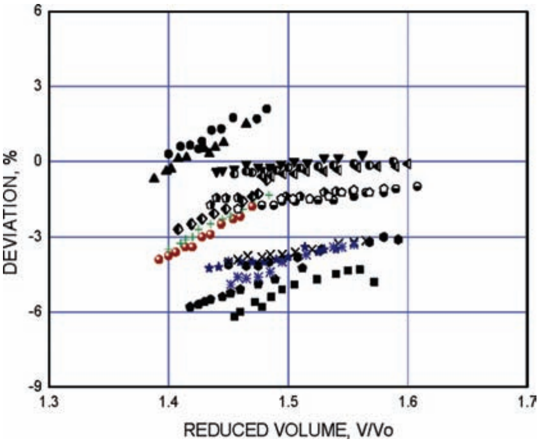

Figure 6. Deviations of the experimental data for the thermal conductivity for water, 2-*n*-butoxyethanol, and their mixtures from their predictions of the scheme of Assael, Dymond, and their collaborators.[16–20] Water: ▲, 304.15 K; ●, 321.15 K. 2-*n*-Butoxyethanol: ▼, 304.15 K; ◐, 321.15 K; half-filled triangle pointing left, 338.15 K. x_1 = 0.0478: red ●, 304.15 K; green +, 317.15 K; half-filled diamond, 320.90 K. x_1 = 0.1732: filled pentagon, 304.15 K; blue ∗, 321.15 K; ■, 335.15 K. x_1 = 0.5000: blue ★, 304.15 K; ×, 321.15 K; ⬢, 344.15 K. x_1 = 0.7500: half-filled pentagon, 304.15 K; ⬠, 321.15 K; ◒, 338.15 K.

Figures 7 to 9 contain plots of the deviations of the experimental data from these representations for individual fluids in order of increasing 2-*n*-butoxyethanol content. The maximum deviation over the whole set is less than ± 1.2 %, while the standard deviation is ± 0.5 % which is broadly consistent with the combined experimental uncertainty in the thermal conductivity and density values.

It is noticeable that the idea of the hard-sphere theory that the temperature dependence of the thermal conductivity lies largely within the density changes and the small changes of V_o are still confirmed for the associating systems studied here. It is equally apparent, for all of the systems studied here,

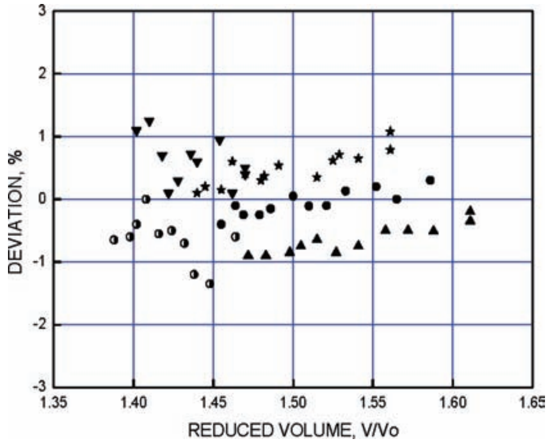

Figure 7. Deviations of the experimental data for the thermal conductivity of water and 2-*n*-butoxyethanol from their representation by means of eq 9 and the coefficients of Table 8. For 2-*n*-butoxyethanol: ∗, 304.15 K; ●, 321.15 K; ▲, 344.15 K. For water: ◑, 304.15 K; ▼, 321.15 K.

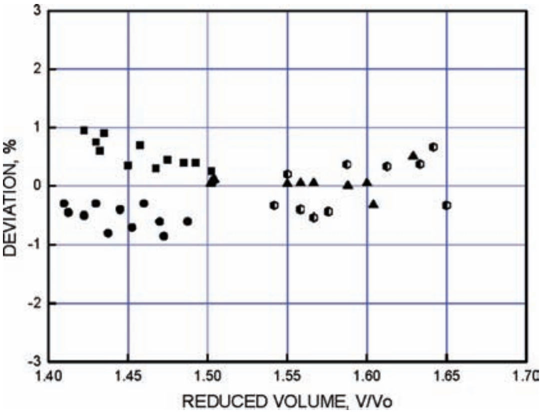

Figure 8. Deviations of the experimental data for thermal conductivity of mixtures of 2-*n*-butoxyethanol and water with mole fraction $x_1 = 0.0478$ and $x_1 = 0.1732$ from their representation by means of eq 9 and the coefficients of Table 8. For $x_1 = 0.0478$: ■, 304.15 K; ●, 317.15 K. For $x_1 = 0.1732$: ▲, 304.15 K; half-filled hexagon, 321.15 K.

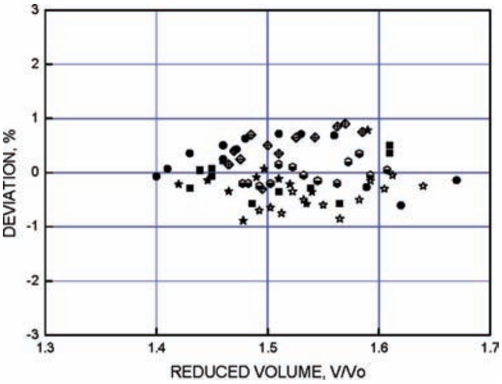

Figure 9. Deviations of the experimental thermal conductivity of mixtures of 2-*n*-butoxyethanol and water with mole fractions $x_1 = 0.5000$ and $x_1 = 0.7500$ from their representation by means of eq 9 and the coefficients of Table 8. $x_1 = 0.5000$: ■ 304.15 K; ●, 321.15 K; ★, 338.15 K. and $x_1 = 0.7500$: diamond with a plus inside, 304.15 K; half-filled hexagon, 321.15 K; ☆, 344.15 K.

that the characteristic molar volume V_o does not decrease with increasing temperature as is expected from the original adaptation of the hard-sphere theory. This is typical of what has been found for polar fluids[20] and, presumably, reflects the effects of strong attractive forces.

Conclusions

New experimental data for the thermal conductivity of aqueous mixtures of 2-*n*-butoxyethanol have been obtained over a wide range of temperatures. The predictive procedure, available based upon the rigid-sphere theory, is able to generate values within the uncertainty claimed for the procedure by Assael et al.[16–20] At a higher level of precision, however, the present experimental data cast yet some doubt upon the universality of the density dependence of the reduced thermal conductivity of liquids. Since the present systems are polar and have hydrogen-bonding present, these observations are not surprising but indicate that a search for a means to incorporate the effects of attractive forces between molecules into the rigid-sphere description of the properties would be valuable. Despite this reservation, it does seem that one of the major attributes of the hard-sphere theory, which isolates the temperature dependence of the thermal conductivity within a hard-core volume, remains intact.

In subsequent work, we intend to explore the extent to which the work of Vesovic and his colleagues on revisions of the scheme of Vesovic and Wakeham to the treatment of transport in liquid mixtures is applicable to the mixture studied here.

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