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Thermal Conductivity of Water and 2-*n*-Butoxyethanol and Their Mixtures in the Temperature Range 305–350 K at Pressures up to 150 MPa[1]

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The thermal conductivity of binary liquid mixtures of water and 2-*n*-butoxyethanol has been measured within the temperature range 305–350 K at pressures up to 150 MPa. The measurements have been carried out with a transient hot-wire instrument suitable for electrically conducting liquids and have an estimated accuracy of ±0.3%. The liquid mixture has a closed-loop solubility and reveals a lower critical solution temperature for a mole fraction of 2-*n*-butoxyethanol of 0.0478 at a temperature of 322.25 K. The results of the measurements reveal a small, but discernible, enhancement of the thermal conductivity of the solution at the critical composition.

KEY WORDS: critical phenomena; mixtures; 2-*n*-butoxyethanol; thermal conductivity; transient hot-wire; water.

1. INTRODUCTION

There has been considerable progress in the understanding of transport processes in liquids and liquid mixtures with the aid of the rigid-sphere theory [1–4]. Independently, the study of the enhancement of transport processes in the vicinity of the gas–liquid critical point [5, 6] and, more recently, in the neighborhood of the Plait point of the gas–liquid critical line [7, 8], has received considerable attention. Relatively little attention has been paid to the behavior of the transport properties in the neighborhood of upper and lower critical solution temperatures. Although there have been studies of the behavior of the viscosity [9] and mutual diffusion

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coefficient [10] in a number of systems, there seems to have been only one previous investigation of the thermal conductivity, by Gerts and Filippov [11].

Here we consider the system 2-*n*-butoxyethanol + water, which has a lower critical solution temperature of 322.25 K, at a pressure of 0.1 MPa. The objectives of the present study are threefold. First, the system provides the opportunity to determine the ability of the rigid-sphere theory to describe the thermal conductivity of a mixture of such polar components far away from the critical solution temperature. Second, it is intended to examine the behavior of the thermal conductivity close to the critical solution temperature. Finally, the combination of these two studies is intended to investigate mechanisms of separating the contribution to the thermal conductivity of the mixture arising from phenomena associated with the critical point from the background behavior of the liquid mixture.

2. EXPERIMENTS

All of the measurements have been carried out in a transient hot-wire instrument described in detail elsewhere [12–14]. The instrument was especially modified for the present work in the manner described earlier [13] in order to be able to study electrically conducting liquids.

The instrument was employed in the normal fashion [15] to make measurements of the thermal conductivity of pure water and pure 2-*n*-butoxyethanol over the temperature range 304–350 K at pressures up to 150 MPa, as well as of four binary mixtures with 2-*n*-butoxyethanol mole fractions of $x_1 = 0.0478$ (the critical composition at 0.1 MPa), $x_1 = 0.1732$, $x_1 = 0.500$, and $x_1 = 0.7500$. The liquid mixtures were prepared from the pure fluids gravimetrically and the mole fraction has an estimated uncertainty of ± 0.0001. The water employed was triply distilled and degassed, whereas the 2-*n*-butoxyethanol was supplied by Fluka Chemicals Ltd. with a purity greater than 99.8%.

The results of the measurements were interpreted with the aid of the full working equations for the transient hot-wire technique using a full set of corrections. For water, the physical properties required to evaluate the corrections have been taken from the equation of state of Haar et al. [16]; for pure-2-*n*-butoxyethanol, from the data of Malhotra and Woolf [17]; and for the mixtures, from a combination of the direct measurements of Malhotra and Woolf for some compositions and those of Wieczorek [8] and Roux et al. [19] for other compositions. The heat capacity of the mixtures has been estimated from the same property of the pure components by taking a mole fraction average. Since the maximum effect of any of the corrections upon the measured transient temperature rise is only

±0.2%, the propagation of errors in the quantities employed in making these corrections is very small, amounting to ±0.1% at most in the thermal conductivity.

The temperature rise employed for the present measurements has typically been 3.0 K. Near the critical solution temperature, however, this figure was reduced to 2.0–2.5 K in order to allow the closest possible approach to the critical point. It has already been demonstrated [13] that it is possible to approach the critical solution temperature of a liquid to within 0.25 K while maintaining perfect conformality between the performance of the instrument and the usual theoretical model of it.

In this context, it is also worthwhile emphasizing the fact that although the experimental method is a transient one, the thermal conductivity determined with it corresponds to that in the absence of a net diffusive flux, that is, to the steady-state thermal conductivity [21].

3. RESULTS

Owing to limitations of space, it is not possible to present numerical values of the thermal conductivity measurements. Figure 1 shows the pressure dependence of the thermal conductivity for the critical composition

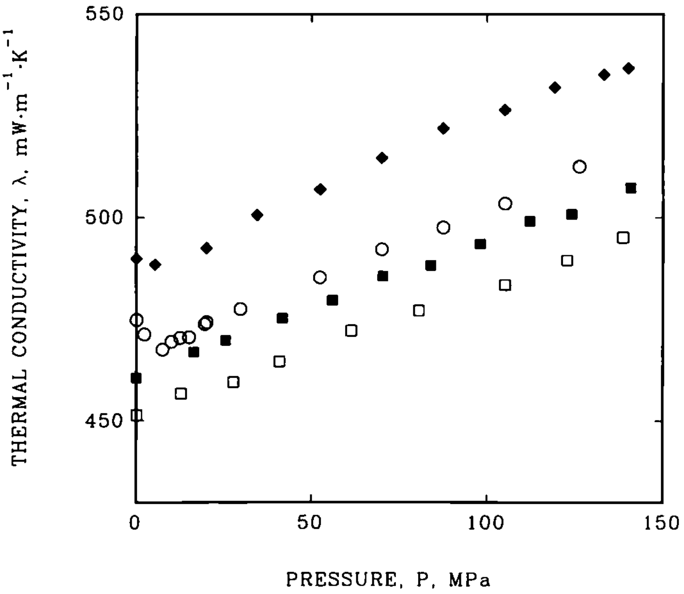

Fig. 1. Pressure dependence of the thermal conductivity of a mixture of 2-*n*-butoxyethanol and water at the critical composition $x_1 = 0.0478$: (□) 304.15 K; (■) 317.15 K; (○) 320.9 K; (◆) 322.0 K.

$x_1 = 0.0478$ for several isotherms. It can be seen that far from the critical solution temperature, the thermal conductivity rises monotonically with increasing pressure in a manner typical of most fluids and fluid mixtures [2, 3]. On the other hand, for temperatures close to the critical solution temperature, an initial decrease in the thermal conductivity is followed by a subsequent increase. This observation is consistent with the fact that as the pressure increases for a fixed temperature, the critical solution temperature rises so that one moves further from it. The decrease in the thermal conductivity initially is therefore to be interpreted as following the decay of a critical enhancement in moving away from the lower critical solution temperature.

Figure 2 shows the composition dependence of the thermal conductivity of the 2-*n*-butoxyethanol + water system for two selected isobars and several isotherms. Two facts emerge from this plot. First, the thermal conductivity of water increases with temperature at constant pressure, while that of 2-*n*-butoxyethanol decreases. Second, for most of the binary mixtures the thermal conductivity depends on temperature rather weakly. However, for the mixture of the critical composition the temperature dependence of the thermal conductivity is even greater than that for water. This last observation is illustrated in more detail in Fig. 3, where the thermal conductivity of the two pure fluids, the equimolar mixture, and the mixture of critical composition are plotted as a function of temperature for a

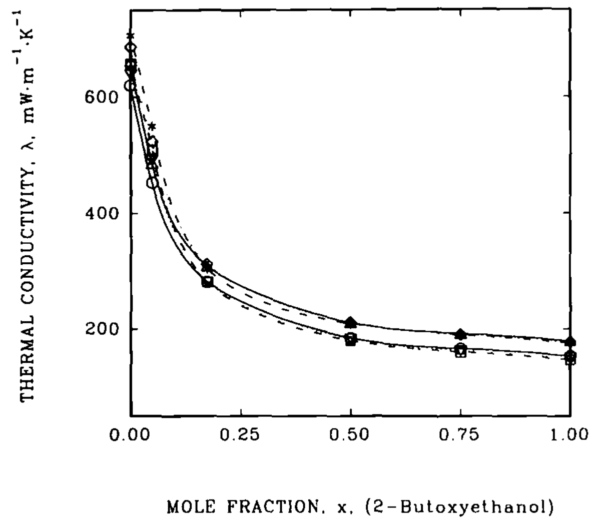

Fig. 2. Composition dependence of the thermal conductivity of a 2-*n*-butoxyethanol + water mixture at 0.1 and 100 MPa for three isotherms. 0.1 MPa: (○) 304.15 K; (▽) 321.15 K; (□) 338.15 K. 100 MPa: (△) 304.15 K; (◇) 321.15 K; (∗) 338.15 K.

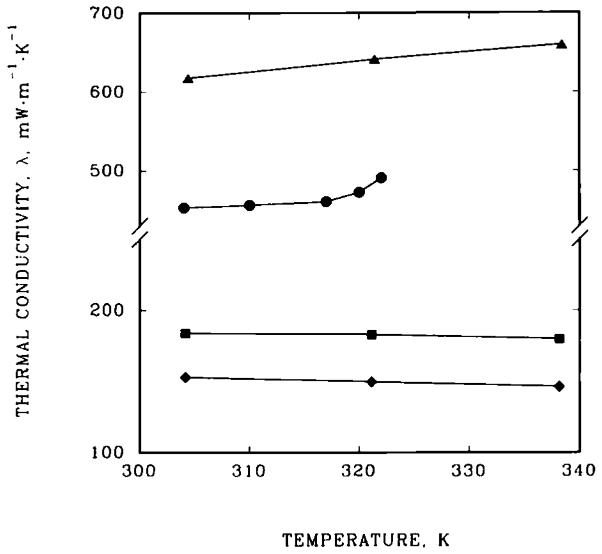

Fig. 3. Temperature dependence of the thermal conductivity of a water + 2-*n*-butoxyethanol equimolar mixture, $x_1 = 0.500$, and a mixture of critical composition $x_1 = 0.0478$ at 0.1 MPa. (▲) Water; (◆) 2-*n*-butoxyethanol; (■) $x_1 = 0.500$; (●) $x_1 = 0.0478$.

pressure of 0.1 MPa. It can be seen that in the vicinity of the critical temperature, 322.25 K, the mixture with the critical composition displays a relatively rapid increase not characteristic of the other systems. This provides further evidence for the existence of a weak enhancement of the thermal conductivity of the mixture in the vicinity of the consolute point.

4. DISCUSSION

In order to seek to describe the behavior of this fluid mixture far away from the lower critical solution temperature, the rigid-sphere theory applied successfully to a wide range of fluids by Assael, Dymond, and their collaborators [22–24] provides the most promising basis.

All applications of the rigid-sphere theory to the representation or prediction of the thermal conductivity of a liquid or liquid mixture are based on the result that for the rough-rigid spheres the dimensionless thermal conductivity

$$\frac{\lambda^*}{R_\lambda} = 1.9362 \times 10^7 \left(\frac{M}{RT}\right)^{1/2} \lambda V^{2/3} \qquad (1)$$

for a particular liquid mixture is a function only of the ratio of the molar volume V to a characteristic molar volume V_0 so that

$$\frac{\lambda^*}{R_\lambda} = F(V/V_0) \qquad (2)$$

Here M is the molar mass of the pure fluid or fluid mixture, T the temperature, and R the universal gas constant. The parameter R_λ accounts for possible internal energy exchange and is known as the roughness factor. Assael et al. [22] have proposed a function $F(V/V_0)$ from a detailed examination of a wide body of experimental data that they suggest may be used for a wide range of fluids, although it is largely based on results for hydrocarbons. For mixtures, they proposed that R_λ and V_0 could be

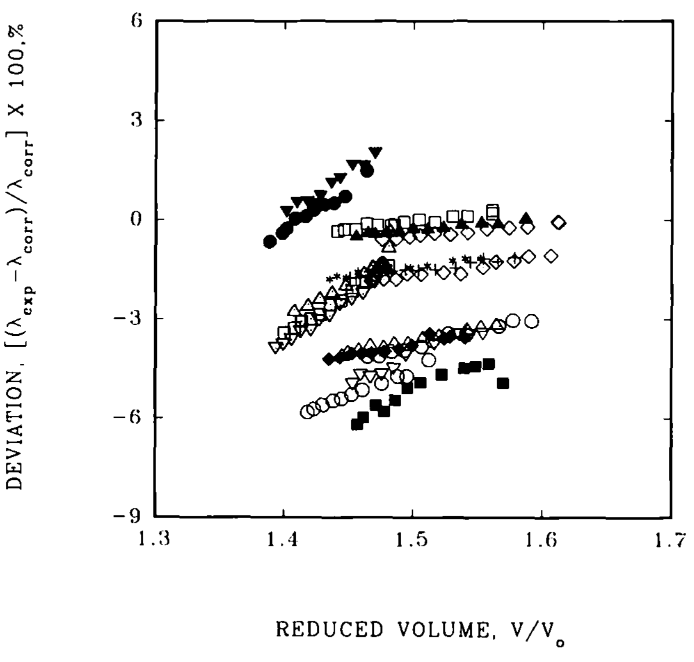

Fig. 4. Deviations of experimental thermal conductivity data of 2-*n*-butoxyethanol, water, and their mixtures from the predictions of the scheme of Assael et al. [22–24]. Water: (●) 304.15 K; (▼) 321.15 K. 2-*n*-Butoxyethanol: (□) 304.15 K; (▲) 321.15 K; ( ) 338.15 K. $x_1 = 0.0478$: (▽) 304.15 K; (⊡) 317.15 K; (△) 320.90 K. $x_1 = 0.1732$: ( ) 304.15 K; (▽) 321.15 K; (■) 335.15 K. $x_1 = 0.5000$: (◆) 304.15 K; (△) 321.15 K; (⊙) 344.15 K. $x_1 = 0.7500$: (∗) 304.15 K; (+) 321.15 K; ( ) 344.15 K.

obtained as mole-fraction averages of the values for the pure components so that

$$R_{\lambda,\,\mathrm{mix}} = x_1 R_{\lambda_1} + (1 - x_1)\, R_{\lambda_2} \qquad (3)$$

and

$$V_{0,\,\mathrm{mix}} = x_1 V_{01} + (1 - x_1)\, V_{02} \qquad (4)$$

In order to test their hypothesis we have determined the values of V_{01} and R_{λ_1} for 2-*n*-butoxyethanol by selecting the values which permit the best representation of the present thermal conductivity data by the function $F(V/V_0)$ given by Assael et al. [22–24]. This has been repeated for pure water. In this process, we have employed the sources of information for the density referred to earlier. Figure 4 shows a plot of the deviations of the thermal conductivity of the pure fluids and the four mixtures from that predicted by the procedure of Assael et al. [22–24]. The results are consistent with the claims by Assael et al. that the procedure has an accuracy of ±6% so that it is suitable for an estimation of the thermal conductivity of the mixtures. It is not, however, sufficiently accurate for the purposes of representing the background behavior of the thermal conductivity of the mixtures in order to extract a thermal conductivity enhancement.

A second attempt to achieve such a representation is to retain the function $F(V/V_0)$ of Assael et al. but to abandon the mixing rules given by Eqs. (3) and (4). This proves to be equally inadequate because, as Fig. 4 shows, the volume dependence of the reduced thermal conductivity of the mixtures is quite different from that of Assael et al. [22–24]. Furthermore, it can be seen from the same figure that the volume dependences of the thermal conductivity of the pure fluids differ considerably from each other so that the representation of the behavior of the system with a single function $F(V/V_0)$ is not possible.

In order to estimate the magnitude of the critical enhancement of the thermal conductivity of the critical composition, we have therefore been forced to use an entirely empirical procedure in which the volume dependence of the thermal conductivity of the mixture of critical composition for all temperatures and pressures far removed from the critical is determined as a function of (V/V_0) by superposition. This function can then be employed to extrapolate the background thermal conductivity into the vicinity of the critical solution temperature. In this way, we have determined that 1.35 K away from the critical solution temperature, the enhancement is 11.9 $\mathrm{mW\,m^{-1}\,K^{-1}}$, which amounts to some 2.5% of the background thermal conductivity.

5. CONCLUSIONS

The present work has demonstrated a weak enhancement in the thermal conductivity of a liquid mixture close to a consolute point. Owing to the fact that the hard-sphere theory is unable to describe the behavior of the background thermal conductivity, it has not been possible to make more than an estimate of the critical enhancement itself.

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