T_g-reduced representation for the α-picHCl + $CoCl_2$ system in Figure 12 insert and see that the expected behavior is realized. The relative fragility of *all* of the liquids of this study can be appreciated from the position of our extreme cases in the overall "strong and fragile liquids" pattern of Figure 12.

Concluding Remarks

This study and its predecessor (*1*) have shown that the consequences, to ion mobility, of complexation processes in ionic liquids, depend on the sort of complex anions which are formed. For fixed charge types, viscosities may increase on complexation if the coordination number in the complex formed is large rather than small (e.g. 6 rather than 4) so that the residual charge on the ligands remains large (e.g., $-^1/_2$ in $CrCl_6^{3-}$ vs $-^1/_4$ in $FeCl_4^-$). This provokes the question of whether similar effects can be seen in the case where the second component cation remains fixed but the coordination number adopted increases due to a smaller ligand size, e.g., NiF_6^{4-} vs $NiCl_4^{2-}$. Experiments designed to test this idea have been carried out and will be reported separately (*12*).

Registry No. α-picHCl, 14401-91-3; $CoCl_2$, 7646-79-9; $NiCl_2$, 7718-54-9; $CdCl_2$, 10108-64-2.

Literature Cited

(1) Angell, C. A.; Elias, A. *J. Phys. Chem.* **1983**, *87*, 4704.
(2) Angell, C. A.; Hodge, I. M.; Cheeseman, P. A. *Molten Salts*; Pensler, J. P., Ed.; The Electrochemical Society: Pennington, NJ, 1976; p 138.
(3) Gammel, P. M.; Angell, C. A. *J. Chem. Phys.* **1974**, *60*, 584.
(4) Elias, A.; Pereira, M. H. *Rev. Port. Quim.* **1973**, *15*, 6.
(5) Smith, G. P. *Molten Salt Chemistry*; Blander, M., Ed.; Interscience: New York, 1964.
(6) Easteal, A. J.; Angell, C. A. *J. Phys. Chem.* **1970**, *74*, 3987.
(7) Angell, C. A.; Shuppert, J. W. *J. Phys. Chem.* **1980**, *84*, 538.
(8) Hodge, I. M. Ph.D. Thesis, Purdue University, 1974.
(9) (a) Angell, C. A. *Relaxations in Complex Systems*; Ngai, K., Wright, G. B., Eds.; National Technical Information Service, U.S. Department of Commerce: Springfield, VA, 1984. (b) Angell, C. A. *J. Non-Cryst. Solids* **1985**, *73*, 1.
(10) Harrap, B. S.; Heymann, E. *Trans Faraday Soc.* **1955**, *51*, 268.
(11) Moynihan, C. T.; Angell, C. A. *Molten Salts*; Mamantov, G., Ed.; Marcel Dekker: New York, 1969; p 315.
(12) Elias, A.; Angell, C. A., to be published.

Received for review July 24, 1986. Revised manuscript received May 22, 1987. Accepted August 10, 1987. We are indebted to the National Science Foundation and the Gulbenkian Foundation for support of this work under Solid State Chemistry Grant No. DMR 8304887.

Supplementary Material Available: Tables of conductivity and kinematic viscosity data for compositions in the three systems of this study [α-picolinium chloride + ($NiCl_2$ or $CoCl_2$ or $CdCl_2$)] (19 pages). Ordering information is given on any current masthead page.

Thermal Conductivities in Seven Ternary Liquid Mixtures at 40 °C and 1 Atm

Richard L. Rowley* and Vernon Gubler

Department of Chemical Engineering, 350 CB, Brigham Young University, Provo, Utah 84602

A transient hot-wire thermal conductivity cell has been used to measure ternary liquid mixture thermal conductivities over the entire composition range at 40 °C and ambient pressure. These data were used to evaluate a previously developed local-composition model for prediction of mixture thermal conductivity. Comparison to the previous results obtained for these systems at 25 °C indicates that, over the small temperature range considered in this work, the local-composition parameters (obtained from the literature from binary vapor–liquid equilibrium) may be considered constant without loss of accuracy.

Introduction

Industrial needs for fluid-mixture thermal conductivity coupled with the variety of mixture compositions and constituencies of possible interest mandates development of an effective multicomponent predictive technique. A local-composition (LC) predictive model for multicomponent thermal conductivity has been reported and tested for binary liquid mixtures (*1*). It is based on the nonrandom two-liquid (NRTL) model (*2*) originally developed for equilibrium properties. As such, the model uses only pure-component thermal conductivities and binary NRTL interaction parameters obtained from vapor–liquid equilibrium (VLE) data of the constituent binary systems. Lack of multicomponent mixture thermal conductivity data has until recently precluded testing of the model for other than binary mixtures.

In order to provide ternary mixture thermal conductivity data against which multicomponent models can be evaluated, we designed and constructed a transient hot-wire thermal conductivity apparatus suitable for accurate measurements of liquid thermal conductivities over a moderate temperature range. The apparatus has been tested and evaluated for pure-component and binary mixture data (*3*). It has also been used to test the efficacy of the LC model for ternary liquid mixtures at 25 °C (*4*). In the latter study, it was found that the model's assumption of binary interactions is adequate and that reasonably accurate predictions can be expected from the model for ternary liquid mixtures with no adjustable parameters. We report here the measurement of ternary mixture thermal conductivities at 40 °C for seven systems. These data indicate that using temperature independent NRTL interactions does not affect the predictions over moderately small temperature ranges.

Experimental Section

The transient hot-wire technique is generally considered to be the most accurate method currently available for measurement of liquid mixture thermal conductivity. It has been employed since the late 1930s and the bulk of the most recent thermal conductivity measurements have been made by this technique. Its history of use, equation derivation, analysis assumptions, experimental techniques, error analysis, assets, and limitations have been carefully studied and are readily available (*5*–*11*).

The thermal conductivity cell used in this work was a single-wire cell, machined from 316 stainless steel and sealed with Viton O-rings. The platinum measurement wire, 0.0005 in. in diameter, was obtained from American Fine Wire Co. with the specifications of 99.95% purity and 266.8 ± 5% Ω/ft. A special cell insert, machined from thin-walled (0.04 inches), 0.50-in.-o.d., stainless steel tubing, was employed to secure and

0021-9568/88/1733-0005$01.50/0 © 1988 American Chemical Society

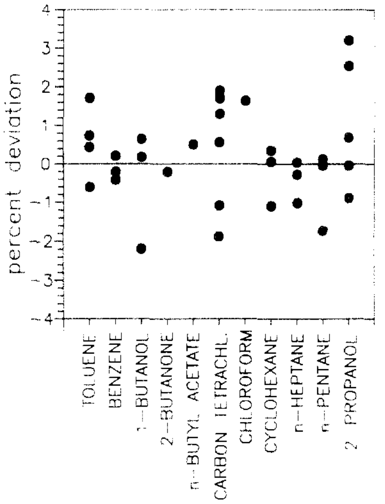

Figure 1. Percent deviation of pure-component thermal conductivity data (over the range 20–40 °C) reported in the literature from those measured in this apparatus. Each point represents an average value reported by a different laboratory.

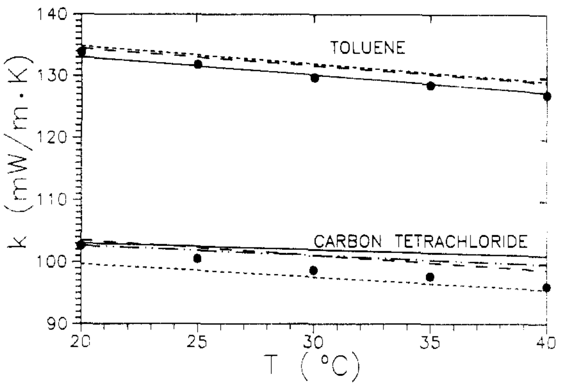

Figure 2. Pure component thermal conductivity of toluene and carbon tetrachloride from 20 to 40 °C. Points represent values measured in this work; lines represent least-squares regression of values reported in ref *12*. The original data for these lines were reported for toluene by Pittman [1968] (—), by Brykov [1970] (- - -), and by Ziebland [1961] (- - -) and for carbon tetrachloride by Tree [1968] (- - -), by Riedel [1951] (- - -), by Mason [1954] (- ·· -), and by Schmidt [1954] (—).

align the wire in its axial position. This secured wire prohibits use of the cell over a wide range of temperatures because of the difference in thermal expansivity of the wire and the insert in which the wire is held. However, the cell is assembled at 25 °C, and at 40 °C the wire should be slightly tauter. Calculations using the linear thermal expansivity of stainless steel and platinum indicate that, for this temperature change, the stainless steel expands 0.022 mm more than the measurement wire. This is less than the tolerance of the original wire positioning. Details of the cell and its operation as well as the data analysis technique have previously been published (*3*, *4*).

The cell has been used to measure pure component thermal conductivities at 25 °C, and the resultant data are generally within the range of values reported by other researchers as shown in Figure 1. Figure 1 illustrates the accuracy of the cell at the same temperature at which it was calibrated. To verify its use at temperatures slightly removed from 25 °C, thermal conductivities of carbon tetrachloride and toluene were measured from 20 to 40 °C; the results are shown in Figure 2. Figure 2 shows a comparison of measured values to best-fit values of the temperature dependence of other investigators' data reported by Jamieson (*12*). As reported earlier (*3*), the pure-fluid studies indicate the accuracy of the instrument to be about 1.0% at the 95% confidence level. Measured values of pure-component thermal conductivities are generally bracketed by values compiled and classified as superior quality by Jamieson (see Figure 1). The average absolute deviation (AAD) between our pure-component measurements and the *average* value from other laboratories for the pure fluids shown in Figure 1 is just under 1.0% with a bias of -0.5%. Since the nemesis of older apparatuses was free convection which raises the measured thermal conductivity, the slightly negative bias is probably not only expected but desired.

In accordance with the infinite line source model in cylindrical coordinates, the temperature rise can be written as (*5*–*11*)

$$\Delta T = \frac{q}{4\pi k}\left[\ln\ t + \ln\left(\frac{4\alpha}{\gamma r^2}\right)\right] \qquad (1)$$

where q is the heat input to the wire by the step-function drive voltage, ΔT is the temperature rise, t is time in seconds, k is thermal conductivity, α is thermal diffusivity, γ = 1.7810, and r is the wire radius. Temperatures were sampled at equal 2-ms intervals over a 800-ms period. From eq 1, thermal conductivity can be obtained from linear least-squares analysis of the slope of ΔT vs ln t and, in principle, thermal diffusivity can be obtained from the intercept. In practice it was found that small imbalances in the Wheatstone bridge at the beginning of the experiment would affect the value of the intercept but not the slope. An error analysis of the apparatus and procedure indicates less than 1% uncertainty in the k values but up to 20% in α values. Since there are better ways to measure α once k is known, we report here only the measured thermal conductivities.

The thermal conductivity was obtained from a linear regression of the ΔT vs ln t data in accordance with eq 1. The first six data points (≤12 ms) were never included in the regression as the finite heat capacity of the wire causes a noticeable error at short times. A wire heat capacity correction by Healy et al. (*9*) was applied and found to be as large as 10% for times under 10 ms, but it rapidly drops to insignificant levels before 40 ms. Other corrections were found to be insignificant because of cell design and the short measurement time. According to the requirements derived by Kierkus et al. (*14*), the infinite heat source assumption is satisfied for our apparatus for wires longer than 13.4 cm. All wires used in the cell were at least 20 cm in length and axial conduction can therefore be neglected. The assumption of a constant heat production rate in the wire was also found to be valid. During the experiment, a 5 K temperature increase resulted in a 1.7% increase in the resistance of the wire and a 0.9% drop in the applied voltage across the wire resulting in a 0.1% change in the heat rate of the wire. As the actual power at each datum point (as opposed to an overall or effective power) was used in the data analysis, the overall effect of the change in wire resistance on the thermal conductivity was found to be less than 0.0025%. Solution of the thermal conduction problem for the wire indicated that the isothermal wire assumption was also valid to about the resolution of our temperature measurements (3 mK maximum radial temperature difference). McLaughlin and Pittman (*8*) and Healy et al. (*9*) have derived geometrical conditions for neglect of bounded medium errors. Over the 8-ms experimental run time, their criteria are satisfied by several orders of magnitude and thermal penetration is much less than the cell radial size. Radiation effects and other end effects were not corrected for, but should be negligible because nearly the same temperature rise (approximately 5 K) was used for each run, and the cell was calibrated for this condition as previously described (*3*, *4*).

Mixtures were prepared volumetrically, mixed in closed flasks at room temperature, and immediately infused into the bottom of the cell until fluid appeared in the waste lines. Fluid was then

Table I. Measured and Calculated Thermal Conductivity for Seven Ternary Systems at 40 °C and Ambient Pressure

w_1	w_2	k(expt), mW/(m·K)	σ	k(LC), mW/(m·K)	dev, %	w_1	w_2	k(expt), mW/(m·K)	σ	k(LC), mW/(m·K)	dev, %
1. Benzene/Carbon Tetrachloride/Cyclohexane											
1	0	135.8	0.01			0.250	0.250	109.7	0.13	112.0	2.1
0	1	96.0	0.04			0.251	0.500	103.2	0.05	106.2	2.9
0	0	114.4	0.13			0.598	0.202	118.0	0.04	119.7	1.4
0.500	0.500	109.6		109.8	0.2	0.400	0.402	108.6	0.06	110.6	1.8
0.498	0	120.4	0.26	124.4	3.3	0.399	0.201	113.3	0.24	116.0	2.4
0	0.500	100.5		103.0	2.5	0.203	0.400	104.8	0.02	107.7	2.8
0.331	0.334	108.9	0.02	111.2	2.1						
2. Cyclohexane/Carbon Tetrachloride/Toluene											
1	0	114.4	0.13			0.155	0.213	115.1	0.43	116.2	1.0
0	1	96.0	0.04			0.201	0.598	99.8	0.05	103.0	3.2
0	0	126.8	0.04			0.598	0.201	109.5	0.01	111.5	1.8
0.500	0.500	100.5		102.7	2.2	0.400	0.399	104.2	0.02	106.8	2.5
0.500	0	117.1		120.9	3.2	0.401	0.199	111.6	0.16	113.9	2.1
0	0.500	106.0		107.9	1.8	0.198	0.399	106.9	0.02	109.0	2.0
0.332	0.335	107.3	0.09	109.7	2.2						
3. 2,2,4-Trimethylpentane/Benzene/Carbon Tetrachloride											
1	0	93.0	0.05			0.200	0.203	93.8	0.01	100.1	6.7
0	1	135.8	0.01			0.200	0.598	111.5	0.04	114.6	2.7
0	0	96.0	0.04			0.611	0.200	95.1	0.02	99.4	4.5
0.499	0.501	106.7	0.11	111.2	4.2	0.395	0.396	101.8	0.08	106.4	4.5
0.502	0	87.8	0.06	94.7	7.9	0.403	0.207	94.0	0.01	99.9	6.3
0	0.500	109.6		109.8	0.2	0.200	0.404	102.4	0.17	106.4	3.8
0.332	0.330	98.7	0.04	103.9	5.3						
4. 2,2,4-Trimethylpentane/Benzene/Cyclohexane											
1	0	93.0	0.05			0.199	0.201	110.5	0.04	112.9	2.2
0	1	135.8	0.01			0.200	0.598	116.5	0.05	121.0	3.9
0	0	114.4	0.13			0.596	0.200	101.0	0.01	103.4	2.3
0.499	0.501	106.7	0.11	111.2	4.2	0.398	0.397	107.5	0.05	111.6	3.8
0.497	0	102.5	0.03	102.5	0.0	0.396	0.201	105.6	0.03	108.0	2.3
0	0.498	120.4	0.26	124.3	3.2	0.204	0.396	112.6	0.06	116.6	3.6
0.332	0.331	108.1	0.08	112.0	3.6						
5. *n*-Hexane/Benzene/Carbon Tetrachloride											
1	0	112.6	0.32			0.201	0.198	98.2	0.06	102.2	4.1
0	1	135.8	0.01			0.199	0.601	117.1	0.08	114.9	-1.9
0	0	96.0	0.04			0.597	0.200	108.0	0.09	110.0	1.9
0.499	0.501	118.3	0.09	119.4	0.9	0.402	0.399	111.6	0.04	112.4	0.7
0.499	0	97.4	0.02	102.2	4.9	0.399	0.199	102.3	0.03	105.7	3.3
0	0.500	109.6		106.8	-2.6	0.200	0.401	107.0	0.15	107.8	0.7
0.334	0.334	106.5	0.05	108.5	1.9						
6. *n*-Heptane/Toluene/Carbon Tetrachloride											
1	0	116.6	0.22			0.202	0.200	99.7	0.04	103.4	3.7
0	1	126.8	0.04			0.200	0.600	116.3	0.03	116.3	0.0
0	0	96.0	0.04			0.604	0.201	114.0	0.72	112.9	-1.0
0.499	0.501	119.9	0.02	121.5	1.3	0.401	0.400	112.9	0.16	114.5	1.4
0.501	0	101.5	0.22	104.3	2.8	0.402	0.201	104.7	0.04	107.8	3.0
0	0.500	106.0		107.6	1.5	0.198	0.403	105.4	0.11	109.2	3.6
0.332	0.331	109.1	0.07	110.2	1.0						
7. *n*-Hexane/Toluene/Carbon Tetrachloride											
1	0	112.6	0.32			0.200	0.200	100.0	0.13	102.7	2.7
0	1	126.8	0.04			0.199	0.599	114.8	0.02	115.7	0.8
0	0	96.0	0.04			0.600	0.204	109.2	0.02	110.7	1.4
0.501	0.500	118.5	0.03	120.0	1.3	0.401	0.400	112.5	0.06	113.2	0.6
0.499	0	97.4	0.02	102.2	4.9	0.400	0.200	104.5	0.46	106.3	1.7
0	0.500	106.0		107.7	1.6	0.199	0.401	105.9	0.01	108.6	2.5
0.329	0.332	108.8	0.23	109.1	2.8						

infused alternately from the top and bottom of the cell to ensure complete removal of all gas bubbles. Measurements were repeated between five and ten times from which a standard deviation was determined. Additionally, some points were checked by refilling the cell with a newly prepared mixture and repeating the thermal conductivity measurements.

Results and Discussion

Seven ternary liquid mixtures were studied at 40 °C and ambient pressure. Generally the thermal conductivity of the pure components, the 50–50 wt % mixture of each of the three binaries, and seven additional ternary compositions were measured for each ternary system. The results of the measurements as well as predicted values using the LC model are shown in Table I. Also shown in Table I is the standard deviation of the replicate measurements made on the same mixture.

The LC model proposed by Rowley (*1*) is

$$k = \sum_{i=1}^{n} w_i k_i + \sum_{i=1}^{n}\sum_{j=1}^{n} w_i w_j G_{ji}(k_{ji} - k_i)/\left(\sum_{l=1}^{n} w_l G_{li}\right) \qquad (2)$$

where k_i represents the pure-component thermal conductivity of component i, w_i is the mass fraction of component i, and G_{ji} ($G_{ij} \neq G_{ji}$ and $G_{ji} = 1$ when $i = j$) are the binary interaction terms which appear in the original equilibrium NRTL model. The cross-interaction thermal conductivity, k_{ij} ($k_{ij} = k_{ji}$), is obtained

Table II. Summary of Average Absolute Deviations at 25 and 40 °C

system[a]	AAD % 25 °C	AAD % 40 °C	max % dev 25 °C	max % dev 40 °C
1	1.9	2.1	3.0	3.3
2	1.4	2.2	2.9	3.2
3	4.8	4.6	9.6	7.9
4	2.8	2.9	4.2	4.2
5	3.9	2.3	4.9	4.9
6	2.3	1.9	3.7	3.7
7	2.8	2.0	4.6	4.9
	2.8[b]	2.6[b]		

[a] System number refers to the identification in Table I. [b] Overall AAD %.

from the pure-component thermal conductivities and the NRTL terms by using the relations

$$k_{ji} = (w_i^* w_{ii}^* k_i + w_j^* w_{jj}^* k_j)/(w_i^* w_{ii}^* + w_j^* w_{jj}^*) \quad (3)$$

$$w_i^* = M_i\sqrt{G_{ji}} \Big/ (M_i\sqrt{G_{ij}} + M_j\sqrt{G_{ji}});$$

$$w_{ii}^* = w_i^* / (\sum_{j=1}^{n} w_j^* G_{ji}) \quad (4)$$

Shown in Table II is a comparison between the AAD for each of the seven systems at 40 °C and that for 25 °C as reported earlier (*4*). In the earlier work, it was found that the binary interactions upon which the LC model is based are adequate for prediction of ternary thermal conductivities. The NRTL parameters used in this study were the same as those used before, taken from the open literature (*15*) where they were reported from regressed VLE data. In general, NRTL constants have been shown to be temperature dependent (*16*). Many of the NRTL parameters were fitted from constant-pressure VLE data and so were not reported at any particular temperature. Others were taken from constant-temperature VLE data. Where multiple sets of parameters at different temperatures were available, the set closest to 25 °C was used as in the previous work. Thus, the comparison between the AAD values in Table II is an indication of the temperature effect of those parameters on thermal conductivity predictions. Table II shows no discernible temperature effect upon the predictions over this small temperature range.

It is of interest to note that only at three compositions were predictions lower than experimental values. The method tends to overpredict ternary thermal conductivity as evidenced here and in the previous study (*3*). This does not occur in binary mixtures (*1*). In all cases that we are aware of, mixture thermal conductivities are lower than the ideal value or mass fraction average of the pure components. Thus, there may be an additional ternary effect, not accounted for by this model, which lowers the thermal conductivity below that predicted solely on the basis of binary interactions.

Conclusions

Mixture thermal conductivities were measured for seven ternary systems at 40 °C and ambient pressure, including the pure-component and binary-limit values. These data were used to test the LC thermal conductivity model for ternary systems at 40 °C; previously only 25 °C tests have been reported. No decrease in the accuracy of the method was observed indicating that, for moderately small temperature ranges, one may consider the NRTL interactions independent of temperature for the purpose of predicting thermal conductivities.

Glossary

G_{ji}	NRTL nonrandomness factor
k	thermal conductivity, mW/(m·K)
k_i	pure component *i* thermal conductivity, mW/(m·K)
k_{ji}	cross-interaction thermal conductivity calculated from eq 3, mW/(m·K)
M_i	molecular weight of component *i*, kg/mol
q	heat flux, W/m^2
r	radius of measurement wire, m
t	time, s
T	temperature, K
w_i	mass fraction of component *i*
w_i^*	mass fraction at which cross interaction is evaluated; calculated from eq 4
w_{ii}^*	local mass fraction at which cross interaction is evaluated; calculated from eq 4

Greek Letters

α	thermal diffusivity, m^2/s
γ	1.7810
σ	standard deviation

Registry No. Benzene, 71-43-2; carbon tetrachloride, 56-23-5; cyclohexane, 110-82-7; toluene, 108-88-3; 2,2,4-trimethylpentane, 540-84-1; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5.

Literature Cited

(1) Rowley, R. L. *Chem. Eng. Sci.* **1982**, *37*, 897–904.
(2) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(3) Rowley, R. L.; White, G. L. *J. Chem. Eng. Data* **1987**, *32*, 63–69.
(4) Rowley, R. L.; White, G. L.; Chiu, M. D. *Chem. Eng. Sci.*, in press.
(5) Held, E. F. M. van der; Drunen, F. G. *Physica* **1949**, *15*, 865.
(6) Horrocks, J.; McLaughlin, E. *Proc. R. Soc. London* **1963**, *A270*, 259.
(7) Parsons, J. R.; Mulligan, J. C. *Rev. Sci. Instrum.* **1978**, *49*, 1460.
(8) McLaughlin, E.; Pittman, J. F. T. *Philos. Trans. R. Soc. London* **1971**, *A270*, 557.
(9) Healy, J. J.; deGroot, J. J.; Kestin, J. *Physica C (Amsterdam)* **1976**, *82C*, 392–408.
(10) Perkins, R. A., Ph.D. Dissertation, Colorado School of Mines, 1983.
(11) Perkins, R. A.; Mohammadi, S. S.; McAllister, R.; Graboski, M. S.; Sloan, E. D. *J. Phys. E.* **1981**, *14*, 1279.
(12) Jamieson, D. T.; Irving, J. B.; Tudhope, J. S. *Liquid Thermal Conductivity: A Data Survey to 1973*; HMO: Edinburgh, 1975.
(13) Pittman, J. F. T. Ph.D. Dissertation, University of London, 1968.
(14) Kierkus, W. T.; Mani, N.; Venart, J. E. S. *Can. J. Phys.* **1973**, *51*, 1182–1186.
(15) Gmehling, J.; Onken, U. *Vapor-Liquid-Equilibrium Data Collection*; Dechema Chem. Data Series; Verlag & Druckerei Friedrich Bishoff: Frankfurt, 1977; Vol. 1.
(16) Skjold-Jorgensen, S.; Rasmussen, P.; Fredenslund, Aa. *Chem. Eng. Sci.* **1980**, *35*, 2389–2403.

Received for review December 23, 1986. Revised manuscript received June 26, 1987. Accepted September 9, 1987.