Diffusion Coefficients for Selected Binary Liquid Systems: Cyclohexanes and *n*-Alkyl Alcohols

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In the present work the integral diffusion coefficients are estimated by using the diaphragm cell technique. The diffusion coefficients are measured at various compositions for two sets of binary systems: one of cyclohexane and *n*-paraffinic alcohols and the other of methylcyclohexane and *n*-paraffinic alcohols. The alcohols used are seven members of homologous series of *n*-paraffinic alcohols from ethanol to octanol. The maximum possible error in the experimental diffusion coefficient could be 8% for both the cyclohexane–*n*-alkyl alcohol system and methylcyclohexane–*n*-alkyl alcohol system. A correlation for each of the two sets of binary systems is given. The maximum deviation in the correlations was less than 6.5 and 3.5% for cyclohexane–*n*-alkyl alcohols and methylcyclohexane–*n*-alkyl alcohols, respectively.

This article reports the experimental determination of the mutual diffusion coefficients for binary systems, along with suitable correlations. The systems studied include two sets of binary mixtures: one of cyclohexane and *n*-paraffinic alcohols and the other of methylcyclohexane and *n*-paraffinic alcohols. The alcohols used are seven members of the homologous series of *n*-paraffinic alcohols from ethanol to octanol.

The diaphragm cell method (*2*) for finding the diffusion coefficients uses Fick's first law and combines the simplicity and accuracy in determining experimentally the diffusion coefficient. Basically the diaphragm cell (Figure 1) consists of a sintered-glass diaphragm (grade G-4) separating two equal-volumed compartments. The volume of each compartment used in this work is 83 ± 0.2 mL with ground-glass joints at either end. By comparison, the volume of the pores of the sintered-glass diaphragm was 1.09 cm^3, negligibly small compared to the volumes of the cell compartments. The liquids in the two compartments were stirred well by two iron-wire-embedded glass stirrers actuated by a rotating magnet. These stirrers wiped twice either side of the diaphragm with each rotation of the magnet and maintained a uniform concentration throughout the compartment. Thus the concentrration gradient was maintained only in the diaphragm. The stirring rate was kept at 40 rpm for all experimental runs.

The diaphragm cell was calibrated at 25 °C by diffusing potassium chloride solution (kept in the bottom compartment) into double-distilled water. The equation used to calculate the integral diffusion coefficients is given by

$$\ln\left(\frac{C^{i}_{B} - C^{i}_{T}}{C^{f}_{B} - C^{f}_{T}}\right) = -\beta t D_{AB} \qquad (1)$$

where D_{AB} is the integral diffusion coefficient. For the calibration, D_{AB} used in eq 1 is determined by

$$D_{I} = \frac{\bar{C}_{B} D_{C_{B}} - \bar{C}_{T} D_{C_{T}}}{\bar{C}_{B} - \bar{C}_{T}} \qquad (2)$$

where

$$\bar{C}_{B} = \tfrac{1}{2}(C^{i}_{B} + C^{f}_{B})$$

$$\bar{C}_{T} = \tfrac{1}{2}(C^{i}_{T} + C^{f}_{T})$$

The parameters D_{C_B} and D_{C_T} are the integral diffusion coefficients that would be obtained in a run of vanishingly short duration at $\bar{C}_B$ and $\bar{C}_T$. The values of D_{C_B} and D_{C_T} are obtained from Woolf and Tilley (*5*).

With known values of $\bar{C}_B$ and $\bar{C}_T$, the average concentrations of the bottom and top compartments, the cell constant β was obtained. Due to the constant rotation and the abrasive action of the stirrers, the diaphragm wears out, causing a change in β. Hence after every 720 h, the cell was recalibrated and the new β was used for further calculations. It was observed that the latter is increased by 2.5% of its initial value of 2057.67 cm^{-2}.

The diffusion runs were conducted for a constant period of 24 h after the equilibrium run of 3 h. The bottom compartment was always filled with liquid of higher density. The temperature was maintained at 25 ± 0.05 °C.

All the chemicals used were of analytical grade except for ethanol, which was purified by the method given in Vogel (*4*). The densities were measured by using an Anton-Paar DMA-55 densitymeter. The densities of pure components are given in Table I, along with the literature values for comparison. Potassium chloride solutions were volumetrically analyzed by using freshly prepared silver nitrate solution.

Composition of solutions were analyzed by an Anton-Paar DMA-55 densitymeter having the accuracy of 0.000 01 g/cm^3. The calibration of density data was done by measuring the densities of mixtures of known composition at 25 °C.

Results

Table II lists the experimental diffusion coefficients of cyclohexane–*n*-alkyl alcohol binary systems, while Table III gives the results for the methylcyclohexane–*n*-alcohol binaries. Each datum point is the average of two runs with a deviation from the average being less than 0.38%.

The maximum possible error in the density determination is 0.1 mol m^{-3}. For all our binary systems the dependence of the density of the mixture on its composition is nonlinear. This leads to error in compositions, C^{i}_{B}, C^{f}_{B}, C^{i}_{T}, and C^{f}_{T}, to about 2 mol m^{-3} at the maximum. For the cell constant, β, it is 5.0 m^{-2}. The maximum error in the determination of time *t*, is of several orders of magnitude less and hence is not used in the calculation of overall error analysis. The resultant maximum possible error in the diffusion coefficient, D_{AB}, is the highest for the methylcyclohexane–propanol system (about 12%) and the lowest for the methylcyclohexane–octanol system (about 3%) and is less than 8% for all the other systems.

Except for the system 1-heptanol–methylcyclohexane, we could not find any report on the experimental determination of diffusion coefficients of these systems in the published literature, and hence no comparative analysis could be made. Robinson et al. (*2*) have reported their experimental D_{AB} values for 1-heptanol–methylcyclohexane in terms of mean concentration (g/cm^3) of the solvent (methylcyclohexane), where mean is taken as the average of the four C^{i}_{B}, C^{f}_{B}, C^{i}_{T}, and C^{f}_{B} terms. On the other hand, we have reported on the basis of the initial mole fraction of the bottom compartment. As their report did

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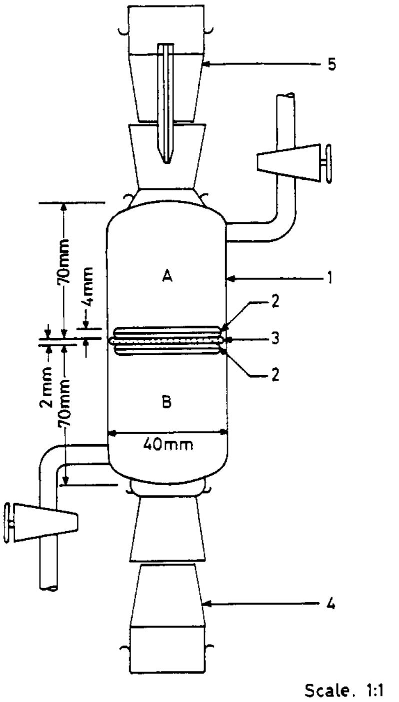
Table I. Physical Properties of the Chemicals Used in the Study at 25 °C

component	molecular weight	ρ_{expt}	$\rho_{lit.}$[a]	molecular volume	$\eta_{lit.}$	η_{expt}	purity, %
ethanol[b]	46.07	0.787 54	0.785 06	59.2	1.10	1.37	99.9
propanol	60.10	0.800 13	0.799 50	81.4	1.97	2.18	99.0
butanol	74.12	0.808 63	0.805 60	103.6	2.60	3.16	99.0
pentanol	88.15	0.811 62	0.811 20	125.8	3.68	3.75	99.8
hexanol	102.18	0.816 35	0.815 60	148.0	4.37	4.83	99.8
heptanol	116.21	0.819 12	0.819 15	170.2	5.68	5.99	99.9
octanol	130.23	0.822 30	0.822 10	192.4	7.21	8.45	99.0
cyclohexane	84.16	0.773 89	0.773 90	118.2	0.84	1.12	99.0
methylcyclohexane	98.18	0.775 00	0.765 06	140.4	0.89	0.88	99.0

[a] Any *Handbook of Physics and Chemistry*. [b] Ethanol is purified from the commercial grade to around 99.9% by using the method prescribed in Vogel (*4*).



Item no.	Name	Specifications
1	Cell	Pyrex
2	Magnetic stirrers	Glass
3	Diaphragm	Porcelain no. 4
4,5	Stoppers	Groundglass B-24

Figure 1. Diaphragm cell.

not give C_B^l, etc., values, we could not convert their data in terms of initial mole fractions of the bottom compartment. However, we converted our data in terms of the mean concentration of the solvent and found that our data deviate from theirs by about 9% on the average, somewhat more than the maximum possible error in our experimental data for the system.

Correlation

The diffusion coefficient data for all compositions of any set of binary systems under study were fitted in the general expression

$$D_{AB} = (A_1 + A_2P_l) + (B_1 + B_2P_l)x + (C_1 + C_2P_l)x^2 \qquad (3)$$

where A_1, A_2, B_1, B_2, C_1, and C_2 are the coefficients for one set of binary systems and x is the mole fraction of cyclohexane. P_l is a dimensionless property defined in terms of molecular weights, viscosities, and molar volumes of solvent and solute as

$$P_l = \frac{(\eta_A V_A / M_A)}{(\eta_B V_B / M_B)} \qquad (4)$$

Table II. Comparison of Experimental and Correlated Diffusion Coefficient Values at 25 °C: *n*-Alkyl Alcohol–Cyclohexane Systems[a]

solvent mole fraction	initial concn difference	diffusion coefficient × 10^6: experimental value	diffusion coefficient × 10^6: from eq 5	% error
	Ethanol–Cyclohexane			
0.0000	9.1956×10^{-3}	7.58	7.40	2.5
0.1937	6.3565×10^{-3}	5.94	5.73	3.6
0.3888	4.2133×10^{-3}	6.13	5.85	4.6
0.5726	2.6341×10^{-3}	7.71	7.60	1.4
0.8056	1.0563×10^{-3}	12.50	12.12	3.0
	Propanol–Cyclohexane			
0.0000	9.1956×10^{-3}	7.05	7.06	−0.1
0.1954	7.0740×10^{-3}	5.55	5.52	0.6
0.3616	5.4107×10^{-3}	5.58	5.54	0.8
0.6237	3.0173×10^{-3}	8.03	8.05	−0.2
0.8054	1.5043×10^{-3}	11.56	11.57	−0.0
	Butanol–Cyclohexane			
0.0000	9.1956×10^{-3}	6.59	6.65	−1.0
0.1846	7.2487×10^{-3}	5.28	5.30	−0.4
0.3818	5.3069×10^{-3}	5.26	5.39	−2.5
0.5849	3.4421×10^{-3}	7.09	7.12	−0.4
0.8047	1.5601×10^{-3}	11.01	10.88	1.2
	Pentanol–Cyclohexane			
0.0000	8.9842×10^{-3}	5.84	6.39	−9.4
0.1954	7.1949×10^{-3}	4.70	5.10	−8.6
0.4174	5.8837×10^{-3}	5.08	5.41	−6.6
0.6116	3.4398×10^{-3}	7.03	7.22	−2.7
0.8107	1.6689×10^{-3}	10.15	10.57	−4.2
	Hexanol–Cyclohexane			
0.0000	9.1956×10^{-3}	5.74	5.93	−3.3
0.1885	7.6516×10^{-3}	4.70	4.83	−2.9
0.3932	5.8837×10^{-3}	4.82	5.02	−4.1
0.5758	4.2200×10^{-3}	6.06	6.38	−5.4
0.7992	2.0630×10^{-3}	9.05	9.60	−6.1
	Heptanol–Cyclohexane			
0.0000	9.1956×10^{-3}	5.11	5.43	−6.3
0.1890	7.8019×10^{-3}	4.44	4.52	−1.9
0.3851	6.2129×10^{-3}	4.53	4.69	−3.7
0.5830	4.4384×10^{-3}	5.70	6.02	−5.5
0.8239	2.0050×10^{-3}	8.85	9.20	−4.0
	Octanol–Cyclohexane			
0.0000	9.1956×10^{-3}	4.64	4.39	5.5
0.1875	7.9379×10^{-3}	4.13	3.87	6.3
0.3876	6.4096×10^{-3}	4.29	4.10	4.4
0.5750	4.7668×10^{-3}	5.36	5.05	5.7
0.8195	2.2333×10^{-3}	7.86	7.35	6.4

[a] % error = 100(*D*(expt) − *D*(calc)/*D*(expt).

where η_A and η_B are the viscosities, V_A and V_B the molar volumes at normal boiling point, and M_A and M_B the molecular weights of solute and solvent, respectively. It can be observed that the dimensions of $(\eta V/M)$ are the same as that of the diffusion coefficient, cm²/s. Hence the above property P_l can be assumed as a reduced diffusion coefficient. The property

Table III. Comparison of Experimental and Correlated Diffusion Coefficient Values at 25 °C: *n*-Alkyl Alcohol-Methylcyclohexane Systems[a]

solvent mole fraction	initial concn difference	diffusion coefficient × 10^6		% error
		experimental value	from eq 6	
Ethanol–Methylcyclohexane				
0.0000	7.7943×10^{-3}	7.01	6.99	0.3
0.1993	5.0415×10^{-3}	5.96	5.96	-0.1
0.4042	3.1321×10^{-3}	5.41	5.50	-1.6
0.5917	1.8852×10^{-3}	5.55	5.59	-0.7
0.7994	8.0007×10^{-4}	6.04	6.28	-4.0
Propanol–Methylcyclohexane				
0.0000	7.7916×10^{-3}	7.46	6.76	9.4
0.1915	5.5477×10^{-3}	5.75	5.88	-2.4
0.4231	3.4595×10^{-3}	5.43	5.51	-1.4
0.6181	2.0700×10^{-3}	5.69	5.78	-1.4
0.8051	9.6744×10^{-4}	6.33	6.53	-3.1
Butanol–Methylcyclohexane				
0.0000	7.7934×10^{-3}	7.10	6.47	8.8
0.1989	5.7869×10^{-3}	5.53	5.73	-3.6
0.4085	3.9671×10^{-3}	5.53	5.53	0.0
0.6131	2.4265×10^{-3}	5.92	5.92	0.1
0.7870	1.2651×10^{-3}	6.66	6.70	-0.5
Pentanol–Methylcyclohexane				
0.0000	9.0898×10^{-3}	6.38	6.29	1.4
0.1929	7.3205×10^{-3}	5.40	5.66	-4.8
0.3810	5.6003×10^{-3}	5.63	5.52	2.0
0.5934	3.6696×10^{-3}	6.15	5.95	3.3
0.7893	1.8967×10^{-3}	6.97	6.88	1.3
Hexanol–Methylcyclohexane				
0.0000	7.7934×10^{-3}	6.16	5.97	3.0
0.1963	6.2337×10^{-3}	5.17	5.50	-6.5
0.3948	4.6724×10^{-3}	5.69	5.55	2.6
0.6100	2.9953×10^{-3}	6.40	6.18	3.5
0.8154	1.4107×10^{-3}	7.34	7.35	-0.0
Heptanol–Methylcyclohexane				
0.0000	7.7910×10^{-3}	5.73	5.62	1.9
0.1804	6.4966×10^{-3}	5.02	5.35	-6.4
0.4085	4.7950×10^{-3}	5.80	5.59	3.6
0.6202	3.1444×10^{-3}	6.57	6.47	2.4
0.8009	1.6794×10^{-3}	7.64	7.57	1.0
Octanol–Methylcyclohexane				
0.0000	7.7910×10^{-3}	4.99	4.90	1.8
0.1998	6.4813×10^{-3}	4.85	5.02	-3.5
0.4399	4.7636×10^{-3}	5.80	5.79	0.2
0.6194	3.3625×10^{-3}	6.79	6.82	-0.4
0.8016	1.8242×10^{-3}	7.99	8.25	-3.3

[a] % error = $100(D(\text{expt}) - D(\text{calc}))/D(\text{expt})$.

value of each binary system is different. The parameters A_1, A_2, B_1, B_2, C_1, and C_2 have been evaluated from the experimental diffusion coefficients by using eq 3. The generalized equation for the cyclohexane system is

$$D_{AB} = (7.89161 - 0.44144P_i) + (-14.56311 + 1.24877P_i)x + (25.84103 - 1.98428P_i)x^2 \quad (5)$$

The calculated and experimental values are tabulated in Table II. The average disagreement between the correlated and experimentally determined values is 3.58%, with the maximum being 6.29%.

Similarly a general equation for the binary systems of methylcyclohexane and *n*-paraffinic alcohols is obtained as given below:

$$D_{AB} = (7.33556 - 0.24556P_i) + (-7.56082 + 0.70014P_i)x + (7.31085 - 0.13330P_i)x^2 \quad (6)$$

where P_i is defined by eq 4 and is a property of the *i*th binary system in methylcyclohexane–*n*-paraffinic alcohol systems. The D_{AB} values are tabulated in Table III. The average disagreement in the predicted and experimental diffusion coefficient values is 2.58%, with the maximum being 3.54%.

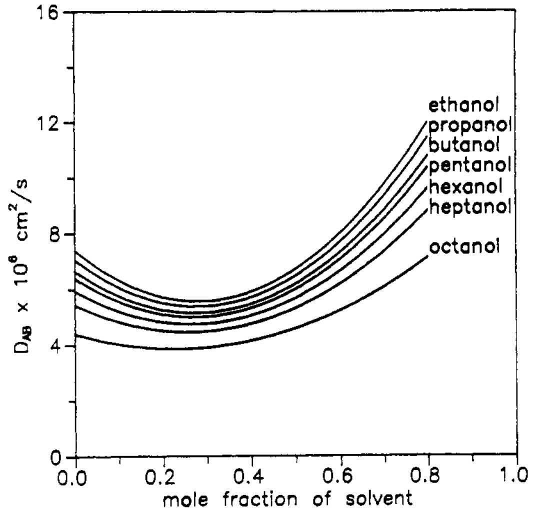


Figure 2. Plots of diffusion coefficients vs mole fraction of the cyclohexane at 25 °C (calculated from eq 5).

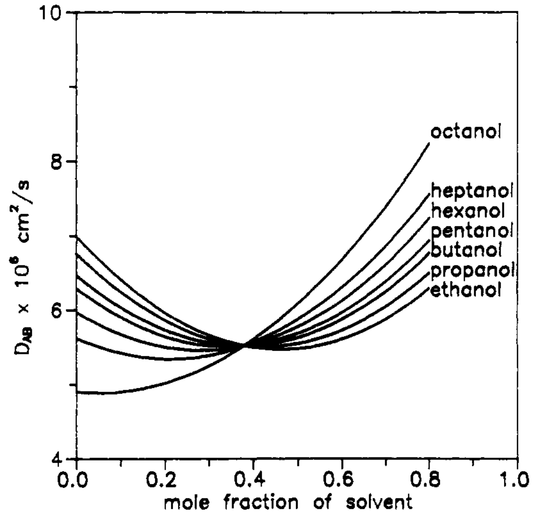


Figure 3. Plots of diffusion coefficients vs mole fraction of the methylcyclohexane at 25 °C (calculated from eq 5).

Plots of D_{AB} vs composition for all the binary systems of cyclohexane and methylcyclohexane with *n*-paraffinic alcohols are given in Figures 2 and 3, respectively. The plots show a U-shaped trend for both series of cyclohexane and methylcyclohexane binary systems. The curve of the ethanol–cyclohexane binary system is the topmost of all the curves, and the octanol–cyclohexane is the lowest one. This is so because ethanol, having the lowest molecular weight of all the alcohols used, has the greatest diffusivity and octanol, being the biggest molecule, is the slowest diffusing. All the curves are parallel, showing the regular gradation in the values of the diffusion coefficient. The curves for ethanol–cyclohexane and ethanol–methylcyclohexane binary systems are more concave than those of other systems because of their higher nonideal nature. As the molecular weight increases, the nonideal nature decreases. Hence the curvature for the diffusion coefficient versus composition curves for the binary systems of higher alcohols is decreasing. The literature (*1*), for binary systems with cyclohexane as one of the components, shows a similar trend of U-shape. It is expected that all the curves of *n*-paraffinic alcohols and cyclohexane binary systems should approach asymptotically to a point when extrapolated to unity of the mole fraction of cyclohexane, the D_{AB} value at that point being the limiting mutual diffusion coefficient of the solutes in cyclohexane.

The graph for the binary systems comprising methylcyclohexane as one component and *n*-paraffinic alcohols as the other is given in Figure 3. The curvature of ethanol–methylcyclohexane is more, while that of the octanol–methylcyclohexane binary system is less, as expected. Further, this figure also shows an interesting feature in that all the curves meet around a single point (approximately at 36% of methylcyclohexane). To the left of the point of intersection the curves show the regular nature; that is, ethanol has a higher value of diffusion coefficient than the others and the gradation can be observed as in the cyclohexane–alcohol binary systems. However, on the right of the point of intersection, the trend is exactly opposite, with the diffusion coefficient values for higher alcohols more than that for the lower alcohols. The values for the diffusion coefficients of methylcyclohexane–alcohol binary systems are lower than those for cyclohexane–alcohol series at corresponding compositions. The present theories of liquid-state diffusion are inadequate to predict the nature of the graph or the values of the diffusion coefficients.

Two features of the present work are to be noted. Firstly, though all *n*-alkyl alcohols from ethanol to 1-octanol are completely miscible with cyclohexane and methylcyclohexane, methanol is not miscible in all proportions. Hence the binary systems methanol–cyclohexane and methanol–methylcyclohexane could not be studied in the present work. Secondly, the density of the binary systems ethanol–cyclohexane, propanol–cyclohexane, and ethanol–methylcyclohexane, for some of the compositions, is lower than either of the pure components. Thus for these systems, whenever the mixture density was lower than that of cyclohexane density, the experiment was conducted by keeping the pure solvent in the bottom compartment.

Conclusion

The correlations given have limitations in that each correlation is applicable only to the system concerned. Further, they do not take care of the temperature effect and hence are applicable only at the temperature used in this work, and finally they cannot be applied to evaluate limiting mutual diffusion coefficients for $x_A \rightarrow 0$ and $x_B \rightarrow 0$, respectively.

Glossary

A_1,A_2	coefficients in eq 3
B_1,B_2	coefficients in eq 3
C_1,C_2	coefficients in eq 3
$\bar{C}_B,\bar{C}_T$	average concentrations in the bottom and top compartments, g/cm^3
C_B^i,C_B^f	concentrations in the bottom compartment, initial and final, respectively, g/cm^3
C_T^i,C_T^f	concentrations in the top compartment, initial and final, respectively, g/cm^3
D_{AB}	mutual diffusion coefficient, cm^2/s
D_{AB}^{∞}	diffusion coefficient at infinite dilution, cm^2/s
D_{C_B}	diffusion coefficient at the bottom compartment average concentration, cm^2/s
D_{C_T}	diffusion coefficient at the top compartment average concentration, cm^2/s
M_A	molecular weight of A
P_i	property used in correlation defined by eq 4
V_A	molar volume, cm^3/g-mol
x	mole fraction of the solvent
β	cell constant, cm^{-2}
η_A	viscosity of component A, g/(cm·s)
η_{expt}	experimentally determined viscosity for pure components, g/(cm·s)
$\eta_{lit.}$	viscosity from literature for pure components, g/(cm·s)
ρ_{expt}	experimentally determined density for pure components, g/cm^3
$\rho_{lit.}$	density from literature for pure components, g/cm^3

Registry No. Ethanol, 64-17-5; propanol, 71-23-8; butanol, 71-36-3; pentanol, 71-41-0; hexanol, 111-27-3; heptanol, 111-70-6; octanol, 111-87-5; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2.

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Vapor–Liquid Equilibria for Four Binary Systems Made of Alcohol and Cyclohexylamine at 100 kPa

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Boiling points for four binary systems made of an alcohol (methanol, ethanol, 1-propanol, or 2-propanol) and cyclohexylamine were measured with a flow-type ebulliometer at 100-kPa pressure, and their isobaric vapor–liquid equilibrium relations were determined.

Introduction

Vapor–liquid equilibria are required for an engineering application such as the design and operation of distillation equipment. Vapor–liquid equilibrium relations can be determined from boiling point curves, which are more easily obtained than conventional equilibrium measurements.

The flow-type ebulliometer was previously proposed for measuring isobaric bubble points (*1*). In the present study, boiling points were measured with the flow-type ebulliometer for the four binary systems made of an alcohol (methanol, ethanol, 1-propanol, or 2-propanol) and cyclohexylamine, and their vapor-phase compositions were determined by the successive calculation method of Tao (*2*) with vapor-phase corrections of Hayden–O'Connell (*3*). Vapor–liquid equilibrium data