Subscripts

i,*j* component numbers

Registry No. C_6H_6, 71-43-2; PhMe, 108-88-3; *m*-xylene, 108-38-3.

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Vapor–Liquid Equilibria at 1 atm for Ternary and Quarternary Systems Composed of Acetone, Methanol, 2-Propanol, and 1-Propanol

Nurbay Gültekin

Faculty of Arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey

The vapor–liquid equilibrium data for each system composed of acetone, methanol, 2-propanol, and 1-propanol at the isobaric condition of 1 atm are presented. The experimental data of the binary systems were used to calculate the binary parameters of the Wilson equation. These binary parameters have been used to calculate vapor-phase compositions and boiling points of related ternary and quarternary systems. Calculated vapor-phase compositions and boiling points have been obtained very close to the experimental data for each system investigated.

Introduction

The usual technique for obtaining vapor–liquid equilibrium data for binary systems is by direct measurement; i.e., equilibrium is established, and phases are sampled and analyzed. However, experimental measurements of vapor–liquid equilibria are quite scarce for multicomponent mixtures. Further, good experimental data are not easily obtained but require considerable experimental skill, experience, and patience. It is, therefore, an economic necessity to consider techniques for calculating vapor–liquid equilibria for multicomponent mixtures. Such techniques must require only a limited amount of experimental information and should be based on a theoretical foundation in order to be reliable for interpolation and extrapolation with respect to temperature, pressure, and composition.

The equation required to calculate vapor–liquid equilibria in multicomponent systems are, in principle, the same as those required for binary systems. In a system containing *N* components, we must solve simultaneously *N* nonlinear equations, applying tedious trial-and-error calculation that can be effectively carried out by an electronic computer (*1*) for each of the *N* components (eq 1).

$$\phi_i y_i P = \gamma_i x_i f_i \qquad (1)$$

For accurate calculation of vapor–liquid equilibria, it is usually necessary to take vapor-phase nonideality into account. This may be done through the use of an equation of state as discussed in numerous references (*2*, *3*). The fugacity coefficient ϕ_i can be calculated by using the equation-of-state rigorous thermodynamic relation (*4*). For pure polar gases, a correlation based on an extended corresponding state theory had been developed by O'Connell and Prausnitz (*5*).

The activity coefficient plays a key role in the calculation of vapor–liquid equilibria. The variation of activity coefficients with composition is best expressed through an auxiliary function g^E, the Gibbs energy defined by

$$G^E = RT\sum_{i=1}^{N} n_i \ln \gamma_i$$

Individual activity coefficients can be obtained from g^E upon introducing the Gibbs–Duhem equation for a multicomponent system at constant temperature and pressure.

$$\sum_{i=1}^{N} n_i \,\mathrm{d} \ln \gamma_i = 0$$

$$RT \ln \gamma_i = (\partial_G{}^E/\partial n_i)_{T,P,n_j} \ (j \neq i)$$

The key problem in calculating a multicomponent vapor–liquid equilibrium is to find an expression for g^E that provides a good approximation for the properties of the mixture. There are different types of expressions for g^E for binary systems can be extended to multicomponent systems (*6*, *7*, *8*). The Wilson equation (*6*) for a multicomponent muxture requires only parameters that can be obtained from related binary mixtures data. This feature provides an important economic advantage since the amount of experimental work required to characterize a multicomponent mixtures is thereby very much reduced. The extension of the Wilson's equation from the binary to the multicomponent case requires no additional assumptions. For a mixture composed of components *i* and *j*, the two parameters

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Table I. Pure-Component Normal Boiling Points T_b and Refractive Indexes

component	T_b(1 atm)/K ref 15	T_b(1 atm)/K measured	n_D(293.15 K) ref 15	n_D(293.15 K) measured
acetone	329.39	329.45	1.3588	1.3579
methanol	337.66	337.60	1.3288	1.3282
2-propanol	355.55	355.65	1.3776	1.3768
1-propanol	370.30	370.30	1.3850	1.3845

Table II. Data of Pure Materials (*1*)

material	T_c/K	P_c/atm	ν_c/(cm^3 g mol^{-1})	ω	ω_H	μ, D	η
acetone	508.7	46.6	213.5	0.309	0.187	2.88	0.00
methanol	513.2	78.5	118.0	0.557	0.105	1.66	1.21
2-propanol	508.2	47.6	247.9	0.984	0.201	1.66	0.00
1-propanol	540.7	51.0	220.0	0.612	0.201	1.68	0.57

Table III. Temperature Dependence of Liquid Molar Volume (cm^3 g mol^{-1}) of Pure Materials

material	T_1/K	ν_1	T_2/K	ν_2	T_3/K	ν_3
acetone	228.15	67.38	273.15	71.48	323.15	76.83
methanol	273.15	39.56	373.15	44.87	473.15	57.94
2-propanol	273.15	75.97	323.15	75.06	373.15	84.52
1-propanol	293.15	74.79	343.15	78.96	393.15	84.52

Table IV. Binary Parameters of the Wilson Equation

i	j	binary system	$\lambda_{ij} - \lambda_{ii}$/(cal g mol^{-1})	$\lambda_{ij} - \lambda_{jj}$/(cal g mol^{-1})
1	2	acetone (1)–methanol (2)	-128.1900	498.9400
1	3	acetone (1)–2-propanol (3)	205.7209	265.4683
1	4	acetone (1)–1-propanol (4)	211.8560	178.8735
2	3	methanol (2)–2-propanol (3)	231.9242	0.1696
2	4	methanol (2)–1-propanol (4)	51.4508	72.8887
3	4	2-propanol (3)–1-propanol (4)	-147.5542	289.4333

Table V. Acetone (1) + Methanol (2) (at 1 atm)

x_1	y_1	Δy	T	ΔT	γ_1	γ_2
0.675	0.706	0.002	328.80	0.05	1.050	1.271
0.625	0.668	0.004	328.92	0.06	1.068	1.231
0.594	0.646	0.002	329.05	0.07	1.081	1.209
0.515	0.589	−0.004	329.54	−0.04	1.120	1.156
0.424	0.521	0.003	330.21	0.05	1.176	1.107
0.386	0.488	−0.002	330.50	−0.02	1.205	1.088
0.332	0.444	−0.001	331.02	−0.03	1.250	1.066
0.314	0.423	−0.001	331.18	−0.07	1.268	1.059
0.257	0.374	−0.002	332.00	0.05	1.325	1.039
0.245	0.363	−0.001	332.11	−0.01	1.338	1.036
0.206	0.322	0.003	332.71	0.04	1.384	1.026
0.168	0.278	0.002	333.31	0.03	1.435	1.017
0.135	0.234	0.002	333.92	0.06	1.482	1.011

mean deviation: MD(T) = 0.050; MD(y_1) = 0.003
root mean square deviation: RMSD(T) = 0.044; RMSD(y_1) = 0.002

Table VI. Methanol (1) + 2-Propanol (2) (at 1 atm)

x_1	y_1	Δy	T	ΔT	γ_1	γ_2
0.195	0.351	0.001	349.60	−0.04	1.149	1.005
0.254	0.432	0.004	348.22	−0.03	1.134	1.009
0.320	0.506	0.008	346.81	−0.06	1.118	1.015
0.385	0.576	−0.006	345.63	−0.05	1.102	1.024
0.486	0.664	−0.005	343.74	−0.08	1.078	1.043
0.515	0.688	−0.009	343.33	−0.07	1.071	1.050
0.585	0.741	−0.011	342.39	0.09	1.055	1.070
0.624	0.768	0.004	341.64	−0.12	1.047	1.084
0.665	0.796	0.005	341.26	0.07	1.039	1.099
0.714	0.828	0.003	340.52	0.03	1.030	1.122
0.775	0.865	−0.007	339.80	0.04	1.020	1.155
0.824	0.892	−0.003	339.22	0.10	1.012	1.189
0.896	0.934	0.003	338.48	0.04	1.005	1.246
0.915	0.947	0.002	338.20	0.06	1.003	1.266

mean deviation: MD(T) = 0.063; MD(y_1) = 0.005
root mean square deviation: RMSD(T) = 0.071; RMSD(y_1) = 0.006

Table VII. Methanol (1) + 1-Propanol (2) (at 1 atm)

x_1	y_1	Δy	T	ΔT	γ_1	γ_2
0.092	0.235	−0.002	365.45	−0.10	0.977	0.999
0.180	0.412	0.001	362.03	0.49	0.982	0.999
0.280	0.562	−0.001	357.05	−0.37	0.988	0.997
0.320	0.610	−0.003	355.68	−0.22	0.990	0.996
0.380	0.675	−0.002	353.40	−0.32	0.993	0.995
0.459	0.753	0.003	351.30	0.27	0.996	0.993
0.581	0.832	−0.003	347.61	0.27	0.999	0.989
0.583	0.835	−0.002	347.42	0.14	0.999	0.989
0.680	0.888	0.001	344.43	−0.21	1.001	0.988
0.764	0.928	0.002	342.55	−0.01	1.001	0.987
0.822	0.940	−0.007	341.45	0.24	1.001	0.988
0.862	0.955	−0.099	340.23	0.04	1.001	0.991

mean deviation: MD(T) = 0.223; MD(y_1) = 0.003
root mean square deviation: MFSD(T) = 0.271; RMSD(y_1) = 0.004

of the Wilson equation Λ_{ij} and Λ_{ji} can be obtained from related binary experimental and pure components data (*1*).

The binary systems of acetone + methanol (*9*), acetone + 2-propanol (*10*, *11*), acetone + 1-propanol (*11*), methanol + 2-propanol (*12*), methanol + 1-propanol (*13*), 2-propanol + 1-propanol (*11*, *14*), and the ternary system of acetone + 2-propanol + 1-propanol (*11*) had been investigated previously. The other ternary systems and quarternary system have been investigated in this study. The binary Wilson's parameters have been determined by using our binary experimental data and those taken from literature (*1*, *11*).

Experimental Section

Purity of Components. The acetone, methanol, 2-propanol, and 1-propanol used in this study were pure-grade materials obtained from E. Merck Actiengesellschaft, Darmstadt, FRG. The physical constants for the materials appear in Table I.

Apparatus and Procedure. The apparatus has been described (*11*). The samples of the vapor and liquid phases were analyzed by using a Perkin-Elmer Model 154-C gas chromatograph equipped with a Superlcowax 10 column (column temperature, 50 to 120 °C at 4 °C/min; flow rate, 5 mL/min of He (flow controlled)). The vapor-liquid equilibrium compositions were determined from the calibration curve by applying a linear interpolation technique (*16*).

Binary Systems. The binary systems composed of acetone, 2-propanol, and 1-propanol had been investigated by Gültekin (*11*). The binary systems acetone + methanol, methanol + 2-propanol, and methanol + 1-propanol have been studied in this work to determine binary parameters of the Wilson's equation.

The experimental and pure-components data (Tables II and III) of these binary systems were used to calculate the binary parameters of the Wilson equation (*6*) by using the simplex search method (*16*) presented in Table IV. Then, the vapor-phase composition and boiling points of the mixtures were calculated by using these parameters at the same pressure and liquid-phase compositions. The root mean square deviations between experimental and calculated vapor-phase compositions and the measured and calculated boiling points for each system are given in Tables V–VII.

Ternary Systems. The ternary system acetone + 2-propanol + 1-propanol had been investigated previously (*11*). The other three ternary systems have been investigated in this work. To obtain vapor-liquid equilibrium data for ternary or quarternary mixtures for all possible combinations of compositions would require a lot of experimental measurements. In this investigation, the experimental vapor-liquid equilibrium data were obtained for several different compositions for each system (Tables VIII–X). On the other hand, the vapor-liquid

Table VIII. Acetone (1) + Methanol (2) + 2-Propanol (3) (at 1 atm)

x_1	x_2	y_1	y_2	Δy_1	Δy_2	T	ΔT	γ_1	γ_2	γ_3
0.781	0.121	0.826	0.125	0.005	-0.004	329.98	0.06	1.023	1.378	1.573
0.702	0.252	0.740	0.238	-0.006	0.005	329.37	0.07	1.041	1.298	1.544
0.579	0.232	0.686	0.226	0.004	-0.007	331.52	-0.05	1.091	1.223	1.340
0.526	0.355	0.622	0.324	0.008	-0.006	330.88	0.06	1.111	1.178	1.354
0.467	0.313	0.600	0.299	-0.003	0.007	332.45	0.08	1.150	1.158	1.126
0.424	0.485	0.535	0.424	0.007	-0.006	331.12	-0.05	1.171	1.115	1.223
0.386	0.279	0.550	0.285	-0.008	0.001	334.97	-0.02	1.216	1.140	1.167
0.332	0.430	0.470	0.417	-0.011	0.009	334.24	0.08	1.246	1.097	1.190
0.314	0.401	0.461	0.401	-0.012	0.008	335.06	-0.05	1.267	1.098	1.161
0.245	0.542	0.522	0.513	-0.007	0.009	335.10	0.07	1.326	1.060	1.178
0.257	0.536	0.389	0.512	-0.009	0.008	334.92	0.05	1.314	1.063	1.184
0.206	0.603	0.329	0.578	-0.009	0.009	335.27	-0.02	1.368	1.046	1.184
0.168	0.672	0.278	0.641	-0.009	0.008	335.41	0.08	1.416	1.032	1.199
0.135	0.753	0.235	0.708	-0.005	0.006	335.33	0.04	1.463	1.019	1.233

root mean square deviation: RMSD(T) = 0.061; RMSD(y_1) = 0.008; RMSD(y_2) = 0.007
mean deviation: MD(T) = 0.056; MD(y_1) = 0.007; MD(y_2) = 0.007

Table IX. Acetone (1) + Methanol (2) + 1-Propanol (3) (at 1 atm)

x_1	x_2	y_1	y_2	Δy_1	Δy_2	T	ΔT	γ_1	γ_2	γ_3
0.082	0.332	0.241	0.504	0.006	-0.008	349.56	0.03	0.541	0.994	1.000
0.102	0.385	0.271	0.533	0.007	-0.007	346.79	0.05	1.512	0.999	1.001
0.119	0.432	0.291	0.554	0.006	-0.006	344.50	-0.07	1.487	1.003	1.002
0.147	0.477	0.319	0.566	0.001	0.000	341.93	0.02	1.448	1.009	1.005
0.163	0.512	0.329	0.577	-0.001	0.001	340.45	0.07	1.427	1.013	1.007
0.185	0.569	0.337	0.599	-0.007	0.007	338.32	0.02	1.400	1.020	1.009
0.209	0.607	0.355	0.601	-0.006	0.006	336.68	-0.04	1.371	1.026	1.013
0.249	0.643	0.380	0.592	-0.009	0.004	334.76	0.05	1.328	1.037	1.020
0.276	0.483	0.457	0.484	0.008	-0.003	336.45	-0.05	1.302	1.041	1.036
0.314	0.512	0.476	0.484	-0.003	0.004	334.51	-0.03	2.265	1.056	1.046
0.362	0.380	0.555	0.382	0.005	0.002	335.88	-0.06	1.227	1.067	1.071
0.474	0.239	0.678	0.248	-0.005	0.006	335.62	-0.07	1.151	1.108	1.132
0.521	0.369	0.637	0.339	0.011	-0.002	331.72	-0.08	1.120	1.151	1.152
0.621	0.372	0.669	0.330	0.008	-0.003	329.02	-0.07	1.070	1.227	1.217
0.774	0.123	0.847	0.127	0.004	-0.002	330.82	-0.06	1.026	1.335	1.387

root mean square deviation: RMSD(T) = 0.006; RMSD(y_1) = 0.007; RMSD(y_2) = 0.005
mean deviation: MD(T) = 0.051; MD(y_1) = 0.006; MD(y_2) = 0.004

Table X. Methanol (1) + 2-Propanol (2) + 1-Propanol (3) (at 1 atm)

x_1	x_2	y_1	y_2	Δy_1	Δy_2	T	ΔT	γ_1	γ_2	γ_3
0.146	0.465	0.288	0.485	-0.002	-0.006	354.90	0.02	1.048	1.052	1.021
0.195	0.343	0.367	0.360	-0.010	-0.008	354.18	-0.03	1.029	1.078	1.006
0.254	0.374	0.446	0.356	-0.009	-0.005	351.95	0.06	1.038	1.073	1.005
0.320	0.478	0.516	0.405	-0.005	0.013	348.16	-0.05	1.062	1.052	1.013
0.385	0.367	0.590	0.286	-0.009	-0.014	347.87	0.07	1.042	1.079	0.996
0.486	0.192	0.700	0.153	-0.015	-0.006	346.75	0.09	1.018	1.137	0.983
0.522	0.363	0.708	0.252	0.007	-0.003	344.41	0.08	1.044	1.084	0.985
0.571	0.282	0.753	0.198	-0.002	-0.003	344.02	-0.02	1.031	1.112	0.977
0.632	0.351	0.776	0.219	0.006	-0.004	341.72	-0.04	1.042	1.092	0.977
0.683	0.171	0.838	0.117	0.003	-0.002	342.41	-0.03	1.015	1.167	0.971
0.711	0.253	0.832	0.158	-0.004	0.005	340.97	0.05	1.014	1.135	0.968
0.761	0.174	0.871	0.111	-0.003	0.006	340.56	-0.04	1.014	1.178	0.968

root mean square deviation: RMSD(T) = 0.005; RMSD(y_1) = 0.008; RMSD(y_2) = 0.008
mean deviation: MD(T) = 0.048; MD(y_1) = 0.006; MD(y_2) = 0.006

equilibrium data were calculated by using related binary Wilson's parameters. The experimental and calculated results were found to be very close to each other for the vapor-phase compositions and boiling points. The root mean square deviations between experimental and calculated results are shown in Tables VIII–X.

***Quarternary System*.** To obtain vapor-liquid equilibrium data for the quarternary mixture for all possible combinations of compositions would also require a lot of experimental measurements. The prediction of the vapor-liquid equilibrium data for the quarternary system from the related binary parameters is an economic way. In this investigation, the experimental vapor-liquid equilibrium data were obtained for several different compositions for controlling predicted results. The root mean square deviations between experimental and calculated results are shown in Table XI.

***Vapor Pressure*.** The vapor pressures of these four components have been reported extensively in the literature for the temperature range required (*17*). An equation was needed description in vapor pressure with temperature for use in the digital computer programs written for the treatment of experimental results. The type of the equation proposed by Riedel (*18*) was used. The constants of the modified Riedel equation were determined by Gültekin (*19*) for many organic compounds (Table XII).

Conclusion

The Wilson equation was found to be applicable to the binary systems. The ternary and quarternary systems can be well represented by these binary parameters. This feature provides an important economic advantage since the amount of ex-

Table XI. Acetone (1) + Methanol (2) + 2-Propanol (3) + 1-Propanol (4) (at 1 atm)

i	x_i	y_i	Δy_i	T	ΔT	γ_1	γ_2	γ_3	γ_4
1	0.412	0.564	0.004	333.45	−0.06	1.185	1.107	1.282	1.078
2	0.379	0.360	−0.003						
3	0.104	0.052	−0.007						
1	0.287	0.441	0.005	334.31	−0.14	1.285	1.058	1.248	1.021
2	0.518	0.489	−0.008						
3	0.096	0.049	0.007						
1	0.082	0.246	−0.003	351.17	−0.30	1.539	1.009	1.115	1.002
2	0.188	0.316	−0.002						
3	0.182	0.170	−0.005						
1	0.174	0.434	0.001	346.87	−0.26	1.419	1.020	1.128	1.017
2	0.159	0.232	−0.001						
3	0.171	0.136	−0.003						
1	0.135	0.323	0.003	344.12	−0.50	1.484	1.018	1.151	1.002
2	0.329	0.429	−0.010						
3	0.135	0.097	−0.003						
1	0.110	0.261	0.005	342.88	−0.33	1.494	1.015	1.172	0.993
2	0.448	0.552	−0.004						
3	0.107	0.070	−0.009						
1	0.078	0.167	0.005	341.59	−0.46	1.540	1.011	1.191	0.985
2	0.559	0.665	−0.008						
3	0.089	0.058	−0.002						
1	0.198	0.368	0.004	337.84	−0.25	1.383	1.029	1.216	1.004
2	0.506	0.528	−0.006						
3	0.078	0.045	−0.001						
1	0.283	0.461	0.003	339.74	−0.28	1.292	1.050	1.248	1.030
2	0.463	0.458	−0.004						
3	0.063	0.035	0.001						
1	0.212	0.400	0.004	338.57	−0.19	1.369	1.054	1.142	1.009
2	0.381	0.426	−0.003						
3	0.242	0.136	−0.001						
1	0.179	0.371	0.001	340.89	−0.28	1.407	1.043	1.133	1.007
2	0.340	0.410	0.001						
3	0.232	0.142	−0.001						

root mean square deviation: RMSD(T) = 0.33; RMSD(y_1) = 0.004; RMSD(y_2) = 0.006; RMSD(y_3) = 0.005
mean deviation: MD(T) = 0.23; MD(y_1) = 0.003; MD(y_2) = 0.005; MD(y_3) = 0.004

Table XII. Constants C_i of a Modified Riedel's Equation (*18, 19*) for the Pure Compounds' Vapor Pressure P_i as Function of Temperature T[a]

compound	C_1	C_2	C_3	C_4
acetone	127.130 346	−7 314.733 098	0.026 934	−19.631 473
methanol	333.681 321	−12 933.901 276	0.094 786	−56.233 138
2-propanol	231.069 495	−11 321.845 381	0.057 795	−37.416 913
1-propanol	−21.070 007	−5 197.246 870	−0.018 187	7.070 192

[a] $\ln (P_i/\text{atm}) = C_1 + C_2/(T/\text{K}) + C_3(T/\text{K}) + C_4 \ln (T/\text{K})$.

perimental work required to characterize a multicomponent mixture is thereby very much reduced.

Glossary

C_i	constants of vapor pressure equation
G	Gibbs energy
g	molar Gibbs energy
MD	mean deviation
N	number of components
n	mole number
P	pressure
R	gas constant
RMSD	root mean square deviation
T	temperature
v	molar volume
x	liquid-phase mole fraction
y	vapor-phase mole fraction
Δy	difference between experimental and calculated vapor-phase composition
ΔT	difference between experimental and calculated boiling points

Greek Letters

γ	activity coefficient
λ	interaction parameters
Λ	binary Wilson parameters
μ	dipole moment
ϕ	fugacity coefficient
η	association factor
ω	acentric factor

Subscripts

c	critical constants
E	excess
H	homorph compound
i,j	components i and j
L	liquid phase
P	pressure
T	temperature
V	vapor phase

Registry No. Acetone, 67-64-1; methanol, 67-56-1; 2-propanol, 67-63-0; 1-propanol, 71-23-8.

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Infinite Dilution Diffusion Coefficients of Several Alcohols in Water

Sam F. Y. Li* and Hui M. Ong

Department of Chemistry, National University of Singapore, Singapore 0511

A Taylor dispersion instrument was used to measure the diffusion coefficients of methanol, ethanol, and 1-butanol in water. A correlation scheme based on a free-volume-type expression could be used to represent the experimental data to within experimental uncertainty.

Introduction

Diffusion coefficient measurements are required in a number of engineering applications, in the study of mass-transfer processes and in evaluating theories of diffusion and the liquid state. The Taylor dispersion technique (*1–5*) has in recent years been established as a rapid and accurate method for measuring the diffusion coefficients of liquids. In previous publications (*6*, *7*), we have reported diffusion data for mixtures of alkanes obtained using an instrument based on this technique. In this work, the same instrument was used to measure the diffusion coefficients of a series of alcohols in water at infinite dilution.

The rough hard-sphere theory (*8–10*) has been used extensively for the correlation of diffusion coefficient data for alkane mixtures (*11–14*). In particular, it has been shown that a free-volume-type expression (*11*) derived from the rough hard-sphere theory can be used for correlating and predicting diffusion coefficients of *n*-alkanes. However, the application of this theory to water/alcohol systems has not been examined. It is therefore one of the objectives in this paper to examine the applicability of this theory to these latter systems.

Experimental Techniques

The Taylor dispersion technique is based on the dispersion of a pulse of an injected mixture in a laminar flowing stream of slightly different composition. The ideal model to measure liquid diffusivities consists of an infinitely long straight tube of uniform, circular cross section, radius a_0, through which flows a fluid or a mixture of fluids with physical properties independent of composition, at a mean velocity u_0. Following the injection of a δ-function of another fluid of a different composition at a particular axial location in the tube, the combined action of the parabolic velocity profile and molecular diffusion causes dispersion of the injected material. Under suitable conditions, the measurements of the first two temporal amounts of the distribution of the concentration perturbation a distance L downstream from the point of injection allows the mutual diffusion coefficients of the binary fluid mixture, D_{12}, to be determined according to the following equation (*2*):

$$D_{12} = \frac{A_0}{24\pi\bar{t}_{\mathrm{id}}}\left(\frac{[1 + 4\sigma_{\mathrm{id}}^2/\bar{t}_{\mathrm{id}}^2]^{1/2} + 3}{[1 + 4\sigma_{\mathrm{id}}^2/\bar{t}_{\mathrm{id}}^2]^{1/2} + 2\sigma_{\mathrm{id}}^2/\bar{t}_{\mathrm{id}} - 1}\right)\times \{1/2 + 1/2(1 - \zeta_a)^{1/2}\} \quad (1)$$

Table I. Infinite Dilution Diffusion Coefficients of Methanol, Ethanol, and 1-Butanol in Water

	$10^9 D_{12}$, m^2 s^{-1}		
T, °C	methanol	ethanol	1-butanol
35	1.88	1.53	1.18
40	2.10, 2.19,[a] 2.42[b]	1.69	1.34
45	2.35	1.91	1.47

[a] Easteal and Woolf (*15*). [b] Extrapolated from Matthews and Akgerman (*13*).

Here $A_0 = \pi a_0^2$ is the cross-sectional area of the tube. $\bar{t}_{\mathrm{id}}$ denotes the first raw moment of the distribution and σ_{id}^2 its second central moment. In addition

$$\delta_a = 12.7997\zeta_0 \quad (2)$$

with

$$\zeta_0 = \frac{\bar{u}_0 a_0^2}{48LD_{12}} \quad (3)$$

Diffusion times of the order of 1–2 h were used in the measurements to ensure that the effects due to secondary flow in the diffusion tubes were negligible (*1*, *2*). The injected samples contained less than 0.1 mole fraction of the alcohols as it has been found that, below this concentration, the diffusion coefficients were independent of the concentration of the sample injected.

Results and Discussion

Table I displays the results obtained for the diffusion coefficients of methanol, ethanol, and 1-butanol in water at temperatures 35, 40, and 45 °C. For methanol, previous measurements by Akgerman (*13*) and Easteal and Woolf (*15*) were available for comparison with the present data. The agreement with the data of Easteal and Woolf is within mutual experimental uncertainties whereas the extrapolated data of Matthews and Agkerman were found to be higher than the present data.

Dymond (*16*) has shown that a free-volume-type equation can be used to represent computer calculations for self-diffusivity of rough hard-sphere molecules. Chen et al. (*17*) developed an analogous expression for mutual diffusion in the form

$$D_{12}/T^{1/2} = \beta(V - V_D) \quad (4)$$

where β is a function of the solute and solvent interaction and V_D is a function only of the solvent and represents the molar volume at which diffusivity approaches zero. Therefore, the rough hard-sphere predicts that $D_{12}/T^{1/2}$ would form a straight line when plotted vs molar volume of the solvent. If this relationship holds, then it would be possible to predict D_{12} for a given solute/solvent pair by determining the two constants, β and V_D.