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Mutual Diffusion Coefficients of Binary Liquid Mixtures of Diethyl Oxalate with Ethanol and Butan-1-ol at 293.15, 303.15, and 313.15 K

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The mutual diffusion coefficients of binary liquid mixtures of diethyl oxalate with ethanol and butan-1-ol in the complete mole fraction range were measured by the Taylor dispersion method. Experimental results at 293.15, 303.15, and 313.15 K are reported. The data are fitted by polynomial equations with an average absolute deviation of 1%. These experimental data are also satisfactorily correlated by a recently developed local composition UNIDIF model.

Introduction

Diffusion coefficient data are needed in designing the heat- and mass-transfer processes in chemical industry. In this study, the liquid mutual diffusion coefficients of diethyl oxalate with ethanol and butan-1-ol were measured by the Taylor dispersion method. Diethyl oxalate is used as a specialty chemical for synthetic resin, pharmaceuticals, and dye stuff. It is miscible with alcohol, ethers, and acetates. The density and viscosity of various ester compounds with alcohol are currently undergoing studies at our laboratory.

In this study, the mutual diffusion coefficients of binary liquid mixtures were measured by the Taylor dispersion method. The experimental data were correlated by employing either the Darken or Vignes equation (Reid et al., 1988), an empirical equation based on the free volume theory (Dymond, 1974), and a local composition UNIDIF model (Hsu and Chen, 1998).

Experimental Section

Chemicals. All of the chemicals were high-purity grade purchased from Merck Co. All chemicals were used without further purification. The purity of ethanol was better than 99.9 mass %, and that of butan-1-ol or diethyl oxalate was better than 99.5 and 99 mass %, respectively. The pure compound properties were measured in this study, and the comparisons with literature data are shown in Table 1. The refractive indexes of the pure compounds were measured at (293.15 ± 0.1) K by an Abbe refractometer, Atago 3T, with an accuracy of ±0.0001. The densities of pure chemicals were measured at (293.15 ± 0.01) K using the Anton Paar DMA 60/602 density meter with an accuracy of ±1.0 × 10^{-5} g cm^{-3}.

Apparatus and Procedures. The mutual diffusion coefficients for the binary mixtures were measured using the Taylor dispersion method. The apparatus and operating criteria employed in this study are similar to those shown by previous investigators (Alizadeh and Wakeham, 1982; Rowley et al., 1988; Probstein, 1989; Rutten, 1992). A metering pump (SSI, digital series 2) was used to drive the carrier fluid in a laminar flow. The solution was degassed (Phenomenex, Degassex DG-440) before passing through the pump. The carrier fluid flows through a six-port injection valve (Supelco) at the upstream of the diffusion coil and then flows into a Teflon diffusion tube which was maintained at a constant temperature in a thermostat. The length of the tube is 15.24 m with an internal diameter of 0.793 75 mm and is tempered in a 30 cm coil radius. In the experiment, an injection of a δ function pulse of 10 μL of solute into a solution was made, and the fluid passed through the circular capillary tube in a laminar flow. The injection valve and the diffusion tube were immersed in a water bath. A thermometer (Hart Scientific 1506) with an accuracy of ±0.01 K was used to measure the temperature. Dispersion of the pulse was established through the parabolic velocity profile of the laminar flow. To prevent the secondary flow, the flow rate was controlled at 0.1 mL/min. The concentration gradient was determined by a refractive index detector (JASCO RI-930) with a cell capacity of 10 μL. The instrument has a sensitivity ranging from $^{1}/_{64}$ to 32 × 10^{-8} RIU (refractive index units) and with the linearity of 5 × 10^{-4} RIU, drift of 8 × 10^{-7} RIU/h, and noise of 5 × 10^{-9} RIU. The analog output was transferred to an IBM compatible PC for data analyses by a 12-bit D/A converter (Advantech, PCL-818HG). This design is consistent with the criteria derived by Aris (Alizadeh et al., 1980; Daubert and Danner, 1991).

Table 1. Comparison of the Measured Refractive Indexes and Densities of Pure Fluids in This Work with Literature Data

	n^{D}(293.15 K)		ρ(293.15K)/(g·cm^{-3})		purity
component	exptl	lit.	exptl	lit.	(mass %)
diethyl oxalate	1.4104	1.4101[a]	1.0789	1.0785[a]	>99
ethanol	1.3614	1.3611[b]	0.7893	0.7893[b]	>99.9
butan-1-ol	1.3990	1.3993[b]	0.8101	0.8098[b]	>99.5

[a] Boit, 1973b. [b] Boit, 1973a.

Under the above conditions, the first two temporal moments of the concentration distribution were regressed by a nonlinear least squares program. The corrections due to the finite volumes of the injection loop and the detector cell were also made to the first two temporal moments. The mutual diffusion coefficient, D_{12}, of a binary fluid mixture is then determined by (Alizadeh et al., 1980; Alizadeh and Wakeham, 1982)

$$D_{12} = \frac{{}_{0}^{2}}{24\bar{t}_{id}}\left[\frac{(1 + 4\sigma_{id}{}^{2}/\bar{t}_{id}{}^{2})^{1/2} + 3}{(1 + 4\sigma_{id}{}^{2}/\bar{t}_{id}{}^{2})^{1/2} + 2\sigma_{id}{}^{2}/\bar{t}_{id}{}^{2} - 1}\right]\left\langle\frac{1}{2} + \frac{1}{2}(1 - \delta_{a})^{1/2}\right\rangle \quad (1)$$

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Table 2. Experimental Results of the Mutual Diffusion Coefficients for the Binary System Diethyl Oxalate (1) + Ethanol (2) at Various Temperatures

x_1	10^9D_{12}/ ($m^2 \cdot s^{-1}$)	x_1	10^9D_{12}/ ($m^2 \cdot s^{-1}$)	x_1	10^9D_{12}/ ($m^2 \cdot s^{-1}$)
T = 293.15 K		T = 303.15 K		T = 313.15 K	
0.0000	1.0224	0.0000	1.2939	0.0000	1.6561
0.0995	0.7619	0.0995	0.9403	0.0995	1.2048
0.2009	0.6135	0.2009	0.7637	0.1989	0.9668
0.2987	0.5396	0.2987	0.6978	0.2987	0.8640
0.3999	0.5099	0.3994	0.6934	0.3999	0.8320
0.4961	0.5670	0.4970	0.7307	0.5007	0.8572
0.5989	0.6243	0.5992	0.7633	0.6019	0.8958
0.6956	0.6821	0.6956	0.8366	0.6913	1.0208
0.7990	0.7973	0.7990	0.9654	0.7990	1.1859
0.9000	0.9524	0.9000	1.1305	0.9000	1.3687
1.0000	1.1774	1.0000	1.5104	1.0000	1.7896

Table 3. Experimental Results of the Mutual Diffusion Coefficients for Binary System Diethyl Oxalate (1) + Butan-1-ol (2) at Various Temperatures

x_1	10^9D_{12}/ ($m^2 \cdot s^{-1}$)	x_1	10^9D_{12}/ ($m^2 \cdot s^{-1}$)	x_1	10^9D_{12}/ ($m^2 \cdot s^{-1}$)
T = 293.15 K		T = 303.15 K		T = 313.15 K	
0.0000	0.5882	0.0000	0.7432	0.0000	0.9090
0.1003	0.4119	0.1003	0.5603	0.1003	0.7154
0.2003	0.3231	0.2003	0.4710	0.2003	0.6221
0.2998	0.2943	0.2998	0.4333	0.2978	0.5845
0.4000	0.3066	0.3968	0.4471	0.3968	0.5963
0.5005	0.3580	0.5005	0.5002	0.5005	0.6734
0.5986	0.4221	0.6003	0.5854	0.6003	0.7410
0.7010	0.5162	0.7010	0.6949	0.6993	0.8420
0.7986	0.6289	0.7986	0.8311	0.7988	1.0193
0.9007	0.7651	0.9007	1.0296	0.9007	1.2178
1.0000	0.9376	1.0000	1.2132	1.0000	1.4699

where r_0 is the internal radius of the diffusion tube. $\bar{t}_{id}$ and σ_{id}^2 are the first and the second moments of the distribution, respectively. In addition,

$$\delta_a = 12.7997\zeta_0 \tag{2}$$

$$\zeta_0 = \frac{2\sigma_{id}^2 - \bar{t}_{id}^2 + \{\bar{t}_{id}^4 + \bar{t}_{id}^2\sigma_{id}^2\}^{1/2}}{8\bar{t}_{id}^2 - 4\sigma_{id}^2} \tag{3}$$

Pratt and Wakeham (1975) have derived the first and the second moments of concentration distribution. The moments were determined by the distance between the injection point and the detection point, the mean velocity of the laminar flow, and the variance of the experimental concentration distribution curve.

To test the accuracy of the apparatus, the limiting diffusion coefficient of ethanol in water was measured at 298.15 K. The experimental value of 1.25 × 10^{-9} m^2/s agrees well with those found in the literature (1.24 × 10^{-9} m^2/s (Tominaga and Matsumoto, 1990); 1.25 × 10^{-9} m^2/s (Tyn and Calus, 1975)).

Results and Discussion

The mutual diffusion coefficients were measured over the complete concentration range for two binary mixtures of diethyl oxalate with ethanol and butan-1-ol at 293.15 K to 313.15 K. Experimental results are listed in Tables 2 and 3, respectively. The following polynomial type equation was used to correlate the experimental data

$$D_{12} = \sum_{i=0}^{4} A_i x_1^{\,i} \tag{4}$$

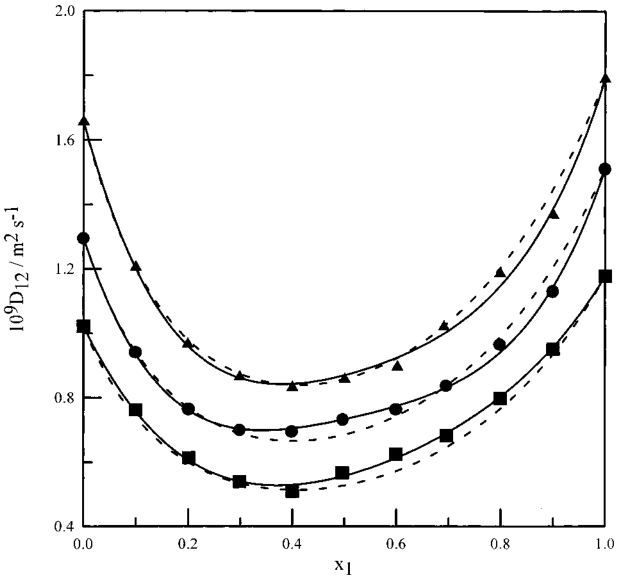

Figure 1. Diffusion coefficients of diethyl oxalate (1) + ethanol (2) as a function of mole fraction of diethyl oxalate (1) (experimental data at (■) 293.15 K, (●) 303.15 K, and (▲) 313.15 K; (solid line) polynomial fit; (dashed line) UNIDIF model).

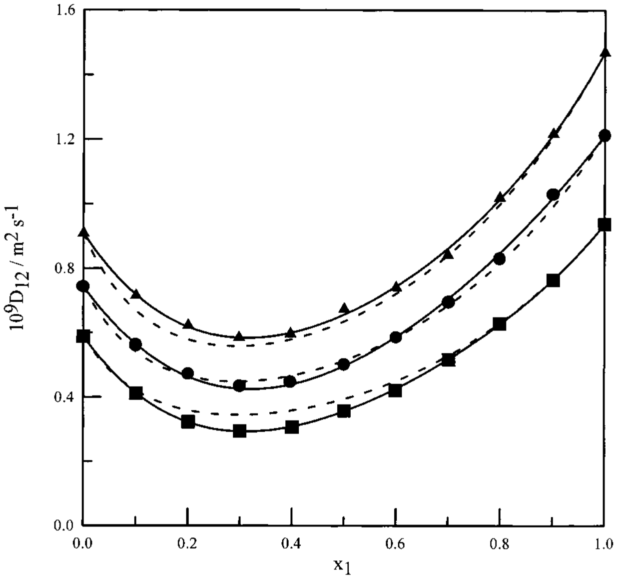

Figure 2. Diffusion coefficients of diethyl oxalate (1) + butan-1-ol (2) as a function of mole fraction of diethyl oxalate (1) (experimental data at (■) 293.15 K, (●) 303.15 K, and (▲) 313.15 K; (solid line) polynomial fit; (dashed line) UNIDIF model).

where A is the optimally fitted parameter and x is the mole fraction. The parameters in this correlation equation were regressed by the least squares method and are shown in Table 4. The polynomial equation satisfactorily correlates the experimental data with an overall absolute average deviation of 1%. Graphical presentations of the experimental data are shown in Figures 1 and 2, respectively. Each curve shows a minimum point of the mutual diffusion coefficients. The minimum points occur at diethyl oxalate mole fraction of 0.4 or 0.3 for the binary mixtures with ethanol or butan-1-ol, respectively. One possible explanation of this result is the formation of hydrogen bonded molecules between alcohol components. The mutual diffusion coefficients decrease due to the increase of effective molecular mass (Cussler, 1984). The other possible explanation is the self-association of nonspherical molecules during the diffusion process (Mills, 1994). This effect also decreases the mutual diffusion coefficients.

Table 4. Regression Results of the Mutual Diffusion Coefficients Using the Polynomial Equation

system	T/K	fitted params, A_i[a]					variance[b]/(10^9 m^2·s^{-1})^2	AAD[c]/%
		A_0	A_1	A_2	A_3	A_4		
diethyl oxalate (1) + ethanol (2)	293.15	1.022	−3.388	7.949	−7.727	3.321	1.4×10^{-4}	1.1
	303.15	1.294	−4.853	14.085	−17.484	8.470	1.9×10^{-4}	0.8
	313.15	1.656	−5.970	15.727	−18.108	8.485	5.8×10^{-4}	1.3
diethyl oxalate (1) + butan-1-ol (2)	293.15	0.588	−2.258	5.520	−4.825	1.912	5.5×10^{-6}	0.4
	303.15	0.743	−2.236	4.723	−2.935	0.918	1.2×10^{-4}	1.2
	313.15	0.909	−2.438	5.804	−4.955	2.150	1.3×10^{-4}	0.7

[a] $D_{12} = \Sigma_{i=0}^{4} A_i {x_1}^i$. [b] Variance, $\sigma^2 = \Sigma(D_{12}^{\text{calc}} - D_{12}^{\text{expt}})^2$/(no. of data points − no. of params). [c] AAD (%) = (100%/(no. of data points))$\Sigma[|D_{12}^{\text{calc}} - D_{12}^{\text{expt}}|/D_{12}^{\text{expt}}]$.

Table 5. Comparison Results of Various Correlative Models of Mutual Diffusion Coefficients at the Temperature Range 293.15 K to 313.15 K

model	T/K	diethyl oxalate + ethanol			diethyl oxalate + butan-1-ol		
		a_{21}/K	a_{12}/K	AAD %	a_{21}/K	a_{12}/K	AAD %
modified Darken[a]							
NRTL(α = 0.2)	293.15	−50.5028	53.3484	5.1	−58.0798	61.4757	14.4
	303.15			6.3			5.7
	313.15			6.0			10.1
UNIQUAC	293.15	75.0555	−1.1792	29.0	186.0061	−102.3657	37.7
	303.15			32.1			27.4
	313.15			34.7			22.1
Vignes[b]							
NRTL(α = 0.2)	293.15	−50.6765	53.5321	5.0	−58.1418	61.5092	14.4
	303.15			6.2			5.7
	313.15			6.0			10.0
UNIQUAC	293.15	74.7916	−1.0862	28.9	186.1304	−103.6586	36.3
	303.15			31.9			25.9
	313.15			34.7			20.7
UNIDIF[c]	293.15	−2.8367	83.7222	3.8	87.0496	−23.9292	7.4
	303.15			2.7			2.4
	313.15			1.6			3.6

[a] Reid et al., 1987. [b] Vignes, 1966. [c] Hsu and Chen, 1998.

Several models have been presented to correlate the composition dependence of the mutual diffusion coefficients. Two commonly used correlation equations are employed in this study. The modified Darken equation (Reid et al., 1987) is expressed as

$$D_{12} = (x_2 D_1^0 + x_1 D_2^0)\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right) \tag{5}$$

where D_1^0 and D_2^0 are the limiting diffusion coefficients of components 1 and 2 at infinite dilution, $(\partial \ln a_1/\partial \ln x_1)$ is the thermodynamic factor, and a_1 is the activity of component 1. The Vignes equation (Vignes, 1966) employs the geometrical average form:

$$D_{12} = (D_1^0)^{x_2}(D_2^0)^{x_1}\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right) \tag{6}$$

In this study, we used either the UNIQUAC or the NRTL activity coefficient model to calculate the thermodynamic factor in the modified Darken or Vignes equation. The nonrandomness factor of the NRTL model was set equal to 0.2. There are two optimally fitted binary parameters in each activity coefficient model.

Recently, a UNIDIF equation for the correlation of the mutual diffusion coefficient has been presented on the basis of the absolute reaction rate theory and the local composition model (Hsu and Chen, 1998). The UNIDIF equation is

$$\begin{aligned} \ln D_{12} = {} & x_2 \ln D_1^0 + x_1 \ln D_2^0 + 2\left\{x_1 \ln\left(\frac{x_1}{\phi_1}\right) + \right. \\ & \left. x_2 \ln\left(\frac{x_2}{\phi_2}\right)\right\} + 2x_1x_2\left\{\frac{\phi_1}{x_1}\left(1 - \frac{\lambda_1}{\lambda_2}\right) + \frac{\phi_2}{x_2}\left(1 - \frac{\lambda_2}{\lambda_1}\right)\right\} + \\ & \{x_2q_1[(1 - {\theta_{21}}^2) \ln \tau_{21} + (1 - {\theta_{22}}^2)\tau_{12} \ln \tau_{12}] + \\ & x_1q_2[(1 - {\theta_{12}}^2) \ln \tau_{12} + (1 - {\theta_{11}}^2)\tau_{21} \ln \tau_{21}]\} \end{aligned} \tag{7}$$

The parameters are defined as

$$\phi_i = \frac{x_i\lambda_i}{\sum_{i=1}^{2} x_i\lambda_i} \tag{8}$$

$$\theta_{ji} = \frac{x_j q_j \tau_{ji}}{\sum_{k=1}^{n} x_k q_k \tau_{ki}} \tag{9}$$

where q_j is the surface area of component j. The interaction parameter τ_{ji} is written as a Boltzmann factor of the binary interaction energy a_{ji}:

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right) \tag{10}$$

For a binary mixture, two binary interaction parameters are optimally fitted from the experimental data.

The optimally fitted binary parameters from various correlation models are shown in Table 5. The absolute

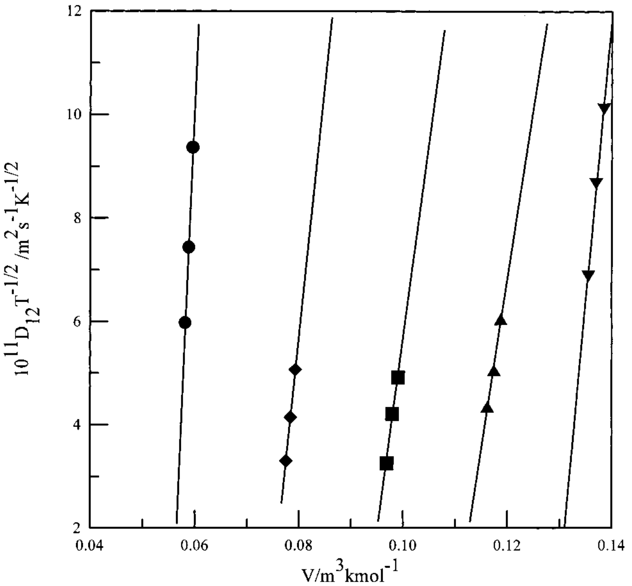

Figure 3. Free volume relation for the system diethyl oxalate (1) + ethanol (2) over the temperature range 293 to 313 K at various mole fractions of diethyl oxalate (1): (●) $x_1 = 0.00$; (◆) $x_1 = 0.25$; (■) $x_1 = 0.50$; (▲) $x_1 = 0.75$; (▼) $x_1 = 1.00$.

Table 6. Regression Results of the Mutual Diffusion Coefficients Using the Free Volume Theory

	fitted parameters			
	diethyl oxalate + ethanol		diethyl oxalate + butan-1-ol	
mole fraction of diethyl oxalate	$\beta \times 10^{11}$/(kmol·m^{-1}·s^{-1}·K$^{-1/2}$)	V_D/(m^3·kmol^{-1})	$\beta \times 10^{11}$/(kmol·m^{-1}·s^{-1}·K$^{-1/2}$)	V_D/(m^3·kmol^{-1})
0.00	2398.48	0.055 712	8912.23	0.0087 626
0.25	983.513	0.074 158	1799.36	0.0397 595
0.50	756.811	0.092 465	1032.8	0.0703 122
0.75	660.856	0.109 645	860.45	0.0999 673
1.00	1092.51	0.129 125	955.549	0.1297 170

average deviations calculated from these models are also compared. Generally, the UNIDIF model yields the best agreement with experimental data. The standard deviation for the repeated measurements is evaluated as 3.0%. The UNIDIF model gives a satisfactory regression result with an overall average absolute deviation (AAD) of 3.6%. Graphical presentations are shown in Figures 1 and 2. The UNIDIF model shows satisfactory composition and temperature dependence for both binary mixtures.

Besides the local composition models, Dymond (1974) has suggested a correlation equation of the mutual diffusion coefficients based on the free volume theory:

$$D_{12}/T^{1/2} = \beta(V - V_D) \tag{11}$$

where β and V_D are two optimally fitted parameters, and the molar volume of the mixture is taken as a simple summation of pure fluid molar volumes (Daubert and Danner, 1991). These parameters are presented in Table 6 for both binary mixtures at various compositions. Graphical presentations are shown in Figures 3 and 4, where a linear relationship is observed. Figure 5 shows a plot of the mutual diffusion coefficients at the infinite dilution condition of alcohol. It also illustrates that the diffusion coefficient approaches zero when there is no free volume of the solute molecule.

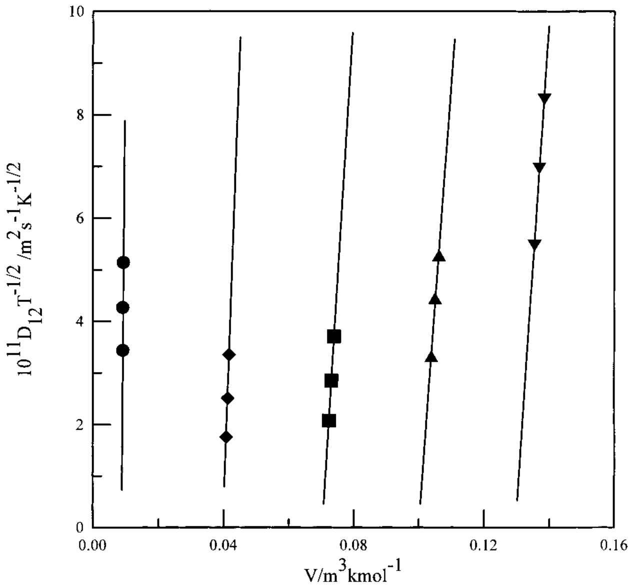

Figure 4. Free volume relation for the system diethyl oxalate (1) + butan-1-ol (2) over the temperature range 293 to 313 K at various mole fractions of diethyl oxalate (1): (●) $x_1 = 0.00$; (♦) $x_1 = 0.25$; (■) $x_1 = 0.50$; (▲) $x_1 = 0.75$; (▼) $x_1 = 1.00$.

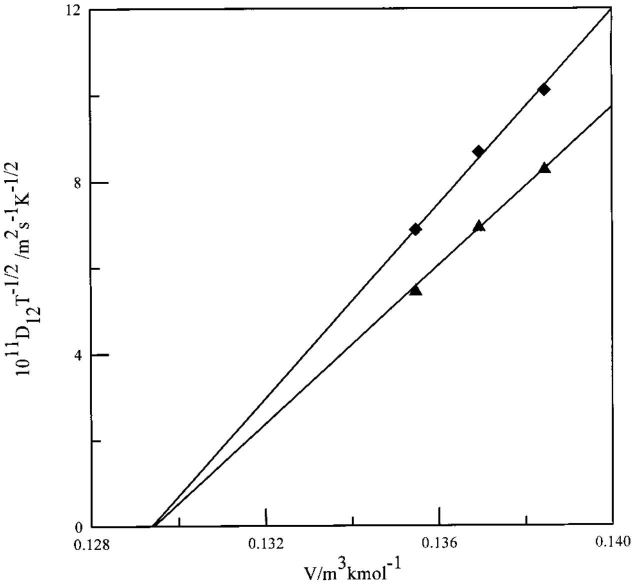

Figure 5. Free volume relation for alcohols in diethyl oxalate over the temperature range 293 to 313 K at infinite dilution of alcohols: (♦) diethyl oxalate (1) + ethanol (2); (▲) diethyl oxalate (1) + butan-1-ol (2).

Conclusion

Experimental mutual diffusion coefficients for the two binary mixtures of diethyl oxalate with ethanol and butan-1-ol are presented at 293.15 to 313.15 K. Various models are employed to correlate the experimental data, and satisfactory results are observed.

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