Applicability of Cullinan's Equation for Liquid Binary Diffusivities

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The purpose of this note is to examine the validity of the equations developed by Cullinan (1985) for calculating mutual diffusion coefficients (D_{12}) in binary liquid solutions. They were originally presented without any comparisons to actual data so that their applicability was unclear. Such comparisons are presented here. The range of mixtures considered spans from those with small deviations from Raoult's law to those having rather large deviations.

One issue is whether it is necessary to restrict the application of the resulting equations to situations in which diffusion occurs by the movement of *clusters* of molecules (rather than single molecules), since that concept was inherent in the derivation. If that were true, one would expect decent results for polar components and less satisfactory predictions for nearly ideal, nonpolar species.

The first equation suggested by Cullinan applied for intermediate compositions, i.e., at which neither component could be considered dilute.

$$\overline{D}_{12\mu}=\frac{kT}{2\pi V^{1/3}}\left[\frac{2\pi x_1 x_2 \alpha_{12}}{1+\alpha_{12}(2\pi x_1 x_2-1)}\right]^{1/2} \tag{1}$$

The second applied at the dilute extreme, which is written here for dilute component 1 in a solvent of component 2.

$$D'_{12\mu}=\sqrt{f^{\circ}_{12}}\, D^{\circ}_{12}\, \mu_2 \frac{V_2^{1/3}}{V^{1/3}}\left[\frac{2\pi x_1 x_2 \alpha_{12}}{1+\alpha_{12}(2\pi x_1 x_2-1)}\right]^{1/2} \tag{2}$$

where

$$\lim_{x_1\to 0}(D_{12}\,\mu)=D^{\circ}_{12}\,\mu_2=\frac{kT}{2\pi V_2^{1/3}}\frac{1}{\sqrt{f^{\circ}_{12}}} \tag{3}$$

and

Table 1. Acetone(1) and Benzene at 25°C

x_1	$\rho^{\dagger}$ 10^3 kg/m^3	α^{*}_{12}	$\mu^{\dagger}$ 10^{-3} kg/m·s	D^{**}_{12} 10^{-9} m^2/s	$\overline{D}_{12}$ 10^{-9} m^2/s	$\overline{R}$ 10^{-9} m^2/s	$\overline{PE}$	D'_{12} 10^{-9} m^2/s	PE'
0.0037	0.877	0.995	0.597	2.750	1.869	0.881	32.03	2.751	-0.04
0.0037	0.877	0.995	0.597	2.740	1.869	0.871	31.78	2.751	-0.40
0.1000	0.868	0.894	0.556	2.580	2.038	0.542	21.01	2.997	-16.16
0.2027	0.859	0.848	0.514	2.550	2.244	0.306	11.99	3.301	-29.45
0.2027	0.859	0.848	0.514	2.560	2.244	0.316	12.33	3.301	-28.95
0.3941	0.842	0.845	0.447	2.700	2.677	0.023	0.86	3.938	-45.85
0.3939	0.842	0.845	0.447	2.690	2.676	0.014	0.51	3.937	-46.36
0.3939	0.842	0.845	0.447	2.700	2.676	0.024	0.87	3.937	-45.81
0.5994	0.825	0.869	0.387	2.980	3.162	-0.182	-6.11	4.651	-56.07
0.5994	0.825	0.869	0.387	2.960	3.162	-0.202	-6.82	4.651	-57.13
0.7808	0.809	0.891	0.345	3.350	3.565	-0.215	-6.42	5.244	-56.54
0.9967	0.790	0.997	0.309	4.140	3.971	0.169	4.07	5.840	-41.06
0.9973	0.790	0.997	0.309	4.180	3.972	0.208	4.97	5.844	-39.81
0.9973	0.790	0.997	0.309	4.150	3.972	0.178	4.28	5.844	-40.82

*Calculated using data from Hirata et al. (1985)
**From Anderson et al. (1958)
†From *International Critical Tables*, III, 143 (1928)

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Table 2. Acetone(1) and Water at 25°C

x_1	$\rho^{\dagger}$ 10^3 kg/m^3	α_{12}^{*}	$\mu^{\dagger}$ 10^{-3} kg/m·s	$D_{12}^{*,**}$ 10^{-9} m^2/s	$\overline{D}_{12}$ 10^{-9} m^2/s	$\overline{R}$ 10^{-9} m^2/s	$\overline{PE}$	D'_{12} 10^{-9} m^2/s	PE'
0.0022	0.996	0.991	0.960	1.280	1.697	−0.417	−32.55	1.241	3.05
0.0831	0.966	0.689	1.304	0.854	1.085	−0.231	−27.03	0.791	7.38
0.2392	0.914	0.288	0.233	0.635	0.810	−0.175	−27.63	1.591	6.93
0.4893	0.855	0.090	0.707	0.819	0.814	0.005	0.67	0.593	27.59
0.6653	0.824	0.231	0.494	1.430	1.612	−0.182	−12.69	1.175	17.83
0.8036	0.806	0.479	0.391	2.390	2.464	−0.074	−3.09	1.797	24.81
0.9265	0.791	0.784	0.337	3.800	3.107	0.693	18.22	2.265	40.39
0.9696	0.787	0.908	0.325	4.560	3.281	0.279	28.04	2.392	47.34

*Calculated using data from Hirata et al. (1985)
**From Anderson et al. (1958)
†From *International Critical Tables*, III, 143 (1928)

$$f_{12}^{o} = 1 - \frac{1}{2\pi} \lim_{x_1 \to 0} \frac{d\alpha_{12}}{dx_1} \tag{4}$$

Significant attributes of Eqs. 1 and 2 are the absence of adjustable parameters and their dependence on limited physical property data (μ, ρ, α_{12}). In addition, Eq. 2 requires the reference value, D_{12}^{o}. Hence, one goal of this study was to determine if the additional information (D_{12}^{o}) provided a significant improvement in accuracy.

Equations 1 and 2 represent modifications and an extension of the concept of Ferrell (1972) and Cussler (1980) who developed the theory of cluster diffusion (movement of groups of molecules) to model nonideal solution behavior. Cussler's ultimate relationship required a reference value of the diffusion coefficient, D_o, and a value for a constant, K. Cussler estimated K for five nonideal solutions from experimental data. He found the value to be sensitive to temperature and to the type of solution. Thus, he did not conclude that one value for K was universally applicable.

Gürkan (1987) reviewed the work of Cussler (1980) and recommended different estimates for K and an empirical exponent, m, which applied to the term that accommodated deviations from thermodynamic ideality. He finally concluded that the use of universal constants for K and m did not appear to be very promising.

Discussion of Results

Since the development of Eqs. 1 and 2 also encompassed ideal solution behavior, the range of applicability should be greater than Cussler's relationship, which was based on the behavior of nonideal solutions only. Hence, we have included, in the evaluation of Eqs. 1 and 2, binary solutions ranging from nearly ideal to highly nonideal.

The scope of this note includes the following solutions:

- Acetone(1) and benzene—25°C
- Acetone(1) and water—25°C
- Carbon tetrachloride(1) and ethanol—25°C
- Bromobenzene(1) and benzene—20°C
- Triethylamine(1) and water—5°C
- Triethylamine(1) and water—15°C

Tables 1 to 6 contain the results of Eqs. 1 and 2 for the above mixtures. The tables also include experimental D_{12} data and values of ρ, α_{12} and μ that were interpolated numerically from published data. The references for all the data are cited as footnotes in the tables. Plotted in Figures 1 and 2 are observed and calculated (via Eq. 1) diffusivities vs. composition for the first and fifth binary solutions.

The results in Tables 1 to 6 show that in general Eq. 1 performed better than Eq. 2, regardless of the extent of ideality. As expected, because of the dependence on D_{12}^{o}, Eq. 2 agrees well with the experimental values at low x_1. But, as x_1 increases,

Table 3. CCl_4(1) and Ethanol at 25°C

x_1	ρ^{*} 10^3 kg/m^3	$\alpha_{12}^{*,**}$	μ^{**} 10^{-3} kg/m·s	$D_{12}^{*,**}$ 10^{-9} m^2/s	$\overline{D}_{12}$ 10^{-9} m^2/s	$\overline{R}$ 10^{-9} m^2/s	$\overline{PE}$	D'_{12} 10^{-9} m^2/s	PE'
0.1000	0.920	0.834	1.090	1.350	1.104	0.246	18.24	1.407	−4.22
0.2000	1.034	0.677	1.078	1.170	1.049	0.121	10.38	1.337	−14.27
0.3000	1.133	0.486	1.051	1.000	0.955	0.045	4.48	1.218	−21.80
0.4000	1.220	0.313	1.013	0.840	0.833	0.007	0.81	1.032	−26.43
0.5000	1.296	0.202	0.969	0.700	0.716	−0.016	−2.32	0.913	−30.43
0.6000	1.365	0.155	0.925	0.600	0.642	−0.042	−7.00	0.819	−2.38
0.7000	1.428	0.132	0.890	0.610	0.579	0.031	5.10	0.738	−20.43
0.8000	1.489	0.125	0.871	0.670	0.505	0.165	24.65	0.644	3.88
0.9000	1.549	0.265	0.874	0.790	0.576	0.214	27.10	0.734	7.09

*From *International Critical Tables*, III, 143 (1928)
**From Hammond and Stokes (1956)

Table 4. Bromobenzene(1) and Benzene at 20°C

x_1	ρ^* 10^3 kg/m^3	α_{12}^{**}	μ^{**} 10^{-3} kg/m·s	D_{12}^{**} 10^{-9} m^2/s	$\overline{D}_{12}$ 10^{-9} m^2/s	$\overline{R}$ 10^{-9} m^2/s	$\overline{PE}$	D'_{12} 10^{-9} m^2/s	PE'
0.0400	0.901	1.004	0.623	1.800	1.964	−0.164	−9.09	1.722	4.33
0.1700	0.982	1.003	0.698	1.850	1.722	0.128	6.92	1.510	18.38
0.3100	1.068	0.992	0.778	1.880	1.521	0.359	19.08	1.334	29.04
0.4500	1.155	0.983	0.859	1.550	1.364	0.186	11.97	1.197	22.77
0.4800	1.173	0.983	0.876	1.350	1.335	0.015	1.09	1.771	−31.19
0.8200	1.384	1.002	1.072	1.300	1.084	0.216	16.65	0.950	26.92
0.9500	1.464	1.005	1.146	1.250	1.015	0.235	18.78	0.890	28.80

*From *Handbook of Chemistry and Physics* (1981-82)
**From Miller and Carmen (1959)

the agreement gets progressively worse. For x_1 greater than 0.1, Eq. 1 agrees with the experimental values significantly better than Eq. 2 in all the cases. Hence, it does not appear that the extra information (D_{12}^0) is beneficial, except at low x_1.

Not only is Eq. 1 superior to Eq. 2 for the systems considered here but the overall performance in predicting D_{12} is very good considering it contains no empirical parameters or diffusivity data. Figure 3 is a plot of the percent error, PE, vs. x_1 for all the six cases. As shown, most of the PE values are within ± 30%, while the average absolute error for x_1 in the range of 0.1 to 0.9 is 12.7%. When the discrepancies between the predicted and experimental values are very large ($|PE| > 30$), Eq. 1 seems to underestimate the experimental values consistently. Otherwise, the collective data appear to be reasonably unbiased, i.e., uniformly scattered about $PE = 0$.

The poorest agreement between experimental and predicted values was for the two triethylamine and water cases. As shown by Tables 5 and 6, agreement was very poor at low x_1 composition (below $x_1 = 0.04$). The 5°C system, however, performed reasonably well for other composition levels. For some x_1 values, the 15°C system also performed well but the average performance was significantly worse than the other systems. This disagreement might be due to the closeness of this solution to the consolute point of about 18°C (Cussler, 1980). At the consolute point, α_{12} and D_{12} are zero. Therefore, near the consolute point, α_{12} and D_{12} are small. Thus, even small measurement errors in α_{12} or D_{12} can produce large percentage deviations between Eq. 1 and D_{12} data.

The case of triethylamine and water at 15°C illustrates the potential consequences of relatively small errors in α_{12} values for nonideal systems. For that case, it was not possible to interpolate the values of α_{12} given by Dudley and Tyrrell (1973b) with confidence. For example, in the graph that they presented, there appeared to be discrepancies in α_{12} of at least 0.02, which could reduce PE from 50 to 10% depending on the concentration level. A sixth-order Redlich-Kister model was used to attempt to fit the data of Kohler (1951). Although all the coefficients were significant at the 99% level, some of the

Table 5. Triethylamine(1) and Water at 5°C

x_1	ρ^{**} 10^3 kg/m^3	α_{12}^{*}	μ^{**} 10^{-3} kg/m·s	D_{12}^{*} 10^{-9} m^2/s	$\overline{D}_{12}$ 10^{-9} m^2/s	$\overline{R}$ 10^{-9} m^2/s	$\overline{PE}$	D'_{12} 10^{-9} m^2/s	PE'
0.0005	0.993	1.000	1.614	0.415	1.216	−0.801	−193.02	0.359	13.49
0.0110	0.985	0.947	2.497	0.285	0.572	−0.287	−100.70	0.169	40.70
0.0195	0.979	0.817	3.213	0.216	1.349	−0.133	−61.66	0.103	52.31
0.0338	0.969	0.373	4.776	0.069	0.128	−0.059	−86.65	0.038	44.93
0.0486	0.958	0.119	6.004	0.050	0.059	−0.008	−16.62	0.017	66.00
0.0753	0.941	0.088	7.551	0.057	0.046	0.011	18.93	0.014	75.44
0.0753	0.941	0.088	7.551	0.054	0.046	0.008	14.16	0.014	74.07
0.0772	0.939	0.088	7.632	0.042	0.046	−0.004	−9.30	0.014	66.67
0.0918	0.930	0.094	8.146	0.046	0.047	−0.001	−2.77	0.014	69.57
0.1119	0.918	0.102	8.568	0.047	0.050	−0.003	−7.01	0.015	68.09
0.1487	0.898	0.115	8.671	0.059	0.056	0.003	4.56	0.017	71.01
0.1900	0.878	0.128	8.088	0.069	0.067	0.002	2.73	0.020	71.01
0.3312	0.826	0.138	4.389	0.119	0.132	−0.013	−10.85	0.039	67.23
0.3312	0.826	0.138	4.389	0.115	0.132	−0.017	−14.70	0.039	66.09
0.4935	0.792	0.103	1.718	0.219	0.279	−0.060	−27.56	0.083	62.10
0.9630	0.742	0.884	0.449	1.602	1.791	−0.189	−11.79	0.529	66.98
0.9630	0.742	0.884	0.449	1.534	1.791	−0.257	−16.74	0.529	65.51

*Dudley and Tyrrell (1973b)
**From Dudley and Tyrrell (1973a)

Table 6. Triethylamine(1) and Water at 15°C

x_1	ρ^* 10^3 kg/m^3	α_{12}^{**}	$\mu^\dagger$ 10^{-3} kg/m·s	D_{12}^{**} 10^{-9} m^2/s	$\overline{D}_{12}$ 10^{-9} m^2/s	$\overline{R}$ 10^{-9} m^2/s	$\overline{PE}$	D'_{12} 10^{-9} m^2/s	PE'
0.0005	0.999	0.998	1.162	0.589	1.317	−0.728	−123.55	0.574	2.55
0.0110	0.989	0.866	1.673	0.364	0.662	−0.298	− 81.86	0.288	20.88
0.0195	0.981	0.738	2.087	0.207	0.475	−0.268	−129.31	0.207	0.00
0.0313	0.970	0.380	2.755	0.069	0.226	−0.157	−226.55	0.099	−43.48
0.0595	0.946	0.038	3.885	0.037	0.056	−0.019	− 51.23	0.024	35.14
0.0918	0.923	0.027	4.594	0.035	0.046	0.012	− 33.60	0.020	42.86
0.1377	0.894	0.036	4.848	0.043	0.057	−0.014	− 31.48	0.025	41.86
0.1900	0.868	0.045	4.490	0.060	0.073	−0.013	− 22.42	0.032	46.67
0.3312	0.822	0.053	2.630	0.124	0.144	−0.020	− 15.79	0.063	49.19
0.4935	0.792	0.069	1.348	0.201	0.305	−0.104	− 51.71	0.133	32.83
0.8456	0.743	0.449	0.475	0.943	1.448	−0.505	− 53.53	0.631	33.09
0.9630	0.733	0.881	0.420	1.885	1.964	−0.079	− 4.18	0.855	54.64
0.9630	0.733	0.881	0.420	1.893	1.964	−0.071	− 3.74	0.855	54.83

*From Dudley and Tyrrell (1973a)
**From Dudley and Tyrrell (1973b)
†From Dudley and Tyrrell (1973a) and Merzline and Tsakolotos data from Timmermanns (1960)

estimated α_{12} values were slightly negative, and so the model was judged to be inadequate. Rather, numerical values were identified by a visual examination of the graph.

In Summary

In absence of diffusivity data, Eq. 1 is recommended for calculating mutual diffusion coefficients for nearly ideal and highly nonideal binary liquid mixtures. No adjustable constants are employed, but its accuracy depends on the accuracy of the necessary density, viscosity and activity data for the mixture. Conversely, Eq. 2 is not recommended unless one wants D_{12} values at low x_1 composition. It is probably less accurate than the former equation due to its reliance on the second derivative of activity coefficient data with respect to composition.

The users of Eq. 1 are cautioned to use accurate α_{12} values at conditions near the consolute point, where the diffusivity drops to zero and extremely nonideal behavior may exist. Other than that, the limitations of Eq. 1 cannot be categorized (say, in terms of dependence on polarity, viscosity, or thermodynamic ideality). For the range of mixtures considered here, no clear trends were observed with respect to deviations from the predictions. We recommend further investigation, perhaps of viscous mixtures and supercritical fluids, to determine the inherent limitations.

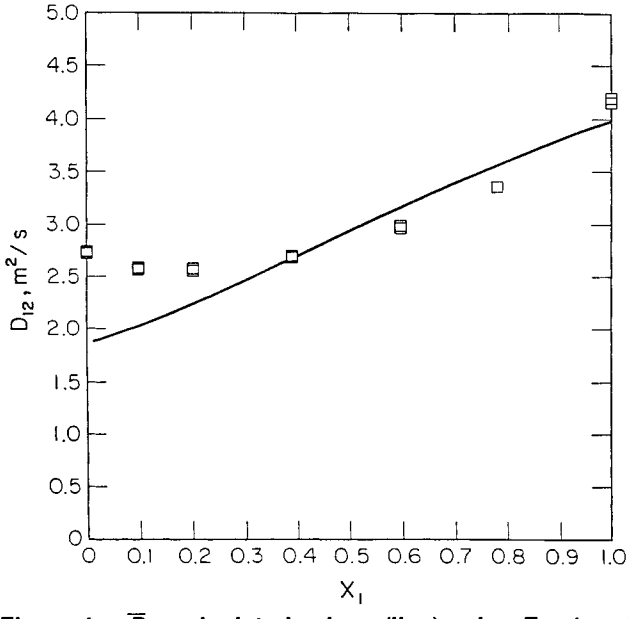

Figure 1. $\overline{D}_{12}$ calculated values (line) using Eq. 1 and experimental values (0) vs. liquid composition for the acetone(1) and benzene system at 25°C.

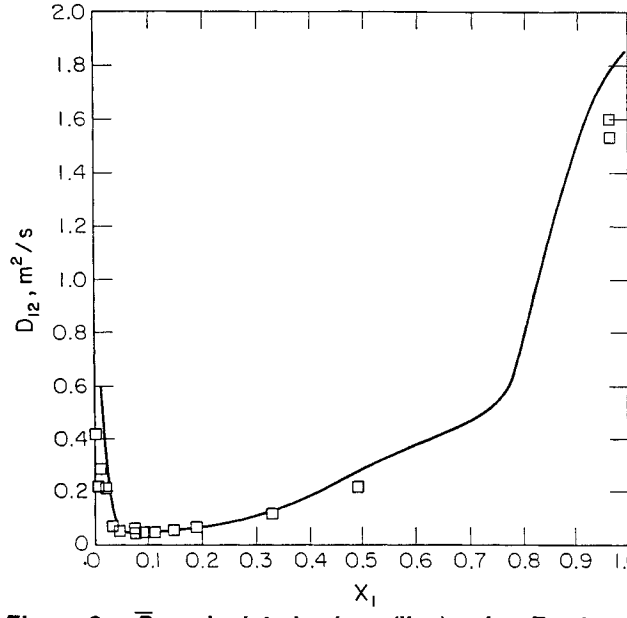

Figure 2. $\overline{D}_{12}$ calculated values (line) using Eq. 1 and experimental values (0) vs. liquid composition for the triethylamine(1) and water system at 5°C.

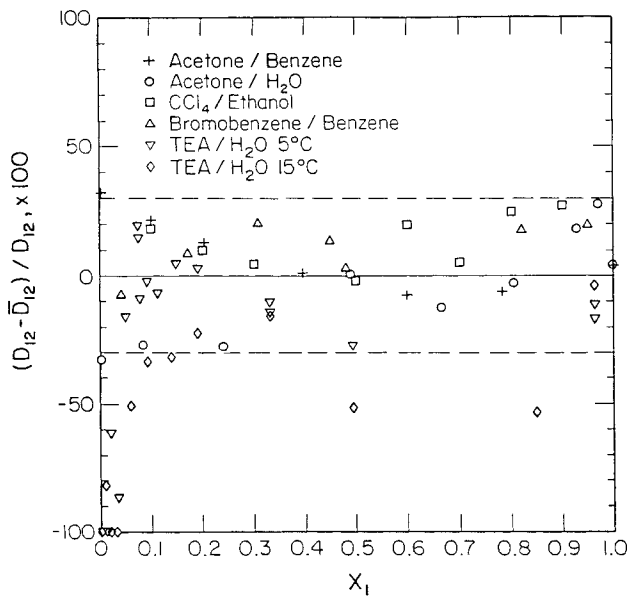

Figure 3. Equation 1 percentage errors, $\overline{PE}$ (from Tables 1 to 6) vs. composition.

Notation

D_{12} = observed binary mutual diffusion coefficient
D_{12} = predicted binary mutual diffusion coefficient, Eq. 1
D'_{12} = predicted binary mutual diffusion coefficient, Eq. 2
D^0_{12} = observed diffusivity of dilute solute(1) in solvent(2)
f^0_{12} = thermodynamic correction, Eq. 4
k = Boltzmann's constant
PE = Eq. 1 percentage error
PE' = Eq. 2 percentage error
R = Eq. 1 residual
T = absolute temperature
V = molecular volume
x_i = mole fraction

Greek Letters

α_{12} = thermodynamic factor $= 1 + \ln\gamma_1/\ln x$
γ_1 = activity coefficient of component 1
μ = viscosity
ρ = density

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