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On the Correlation of Tracer Diffusion Coefficients

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A direct method is described for the correlation and comparison of sets of tracer (or limiting mutual) diffusion coefficients obtained under different conditions of temperature and density, which may or may not overlap, provided that at least one set has been obtained over a range of densities and temperatures. Recommendations are made for sets of diffusion data suitable for the calibration and cross-checking of high-pressure diffusion apparatus, particularly the Taylor dispersion (or chromatographic peak-broadening) apparatus.

Introduction

In a recent paper, Funazukuri *et al.* (1994) reported binary diffusion coefficients of a series of organic compounds in hexane and other solvents. They used the Taylor dispersion technique at moderate pressures. As a check on accuracy, a comparison was made between measurements for benzene and toluene diffusing in hexane and literature data for tracer diffusion coefficients for these systems obtained with the diaphragm-cell method. These diaphragm-cell results were obtained with a high-pressure apparatus for a single isotherm for each system at 298 K to 400 MPa (Dymond and Woolf, 1982), supplemented at atmospheric pressure by higher precision glass diaphragm-cell results again at 298 K and Taylor results between 273 K and 333 K (Dymond, 1981). The high-pressure Taylor dispersion measurements were made between 303 K and 333 K and at 16 MPa and 25 MPa. Funazukuri *et al.* say, " Since these measurement conditions are different, the D_{12} values cannot be compared directly. Thus, the D_{12} data are compared in plots of $T/(\eta D_{12})$ vs solvent molar volume." This indirect procedure combines errors in four experimental quantities in attempting to check one. However a direct method does exist for the comparison of sets of diffusion coefficients (and other transport properties such as the viscosity) obtained under different conditions, which may or may not overlap, provided that at least one set has been obtained over a range of densities and temperatures (Harris, 1982, 1993, 1995). Here, the method is adapted to the case of tracer diffusion and applied to the results of Funazukuri *et al.* (1994) as an example. More importantly, it provides a basis for the calibration and cross-checking of the Taylor dispersion apparatus operated above atmospheric pressure using systems studied by the more established diaphragm-cell method. (Suitable systems for atmospheric pressure calibration, for which precise data are more abundant, have been discussed elsewhere (Harris, 1991).)

Method

Regularities in the dependence of transport properties on molar volume have long been known, dating back more than 80 years to the viscosity studies of Batschinskii (1913). In particular, the fluidity (Φ) and self-diffusion coefficient (D) for simple, non-hydrogen-bonded molecular liquids are almost linear functions of the molar volume at moderate pressures, as are the same properties for the hard sphere fluid as obtained by computer simulation (Dymond, 1974a). At high pressures, $D-V$ (Parkhurst and Jonas, 1975) and $\Phi-V$ (Van Wijk and Seeder, 1937) isotherms curve away from a straight line dependence, real liquids being more fluid than the hard sphere model would predict.

This curvature is conveniently reproduced by the equation (Harris, 1982)

$$D^* = \zeta_1 + \zeta_2 V_{\text{ref}}/(1 + \zeta_3/V_{\text{ref}}) \tag{1}$$

D^* is a reduced diffusion coefficient introduced by Dymond (1974b) as an aid in the application of the hard sphere model to real fluids. V_{ref} is a reference molar volume (see below) and the ζ_i are fitted coefficients. For tracer diffusion D^* is given by

$$D^*_{\text{T2}} \equiv \frac{nD_{\text{T2}}}{(nD_{\text{T2}})^{\infty}}\left(\frac{V}{V_0}\right)^{2/3} \tag{2}$$

(using the notation D_{T2} to indicate the limiting value of the mutual diffusion coefficient D_{12} for the diffusion of a trace of solute 2 in solvent 1). n is the number density, and $(nD_{\text{T2}})^{\infty}$ is the density−diffusion coefficient product for a dilute gas of hard spheres given by the Chapman−Enskog equation in its first (composition independent) approximation (Chapman and Cowling, 1960),

$$(nD_{\text{T2}})^{\infty} = \frac{3}{8\sigma_{12}^{\ 2}}\left(\frac{kT}{2\pi\mu}\right)^{1/2} \tag{3}$$

In this equation, μ is the reduced molecular mass $(m_1m_2/(m_1 + m_2))$, k is Boltzmann's constant, and σ_{12} is the mean diameter of the two species. V_0 in eq 2 is $\sigma_{12}^{\ 3}/\sqrt{2}$. Inspection of these equations shows D_{T2}^* to be independent of σ_{12}, so it is a function of only the molecular masses, temperature and density. For many fluids, the reduced diffusion coefficient isotherms on a D_{T2}^*-V plot are similar in the geometric sense and may be superposed onto a single reference isotherm, T_{ref}, chosen arbitrarily, by the coordinate transformation

$$V_{\text{ref}} = V(1 - \xi_1(T - T_{\text{ref}}) - \xi_2(T - T_{\text{ref}})^2) \tag{4}$$

Self-diffusion data for hexane (Harris, 1982), so reduced, are shown in Figure 1 as an example.

Equation 2 simplifies to

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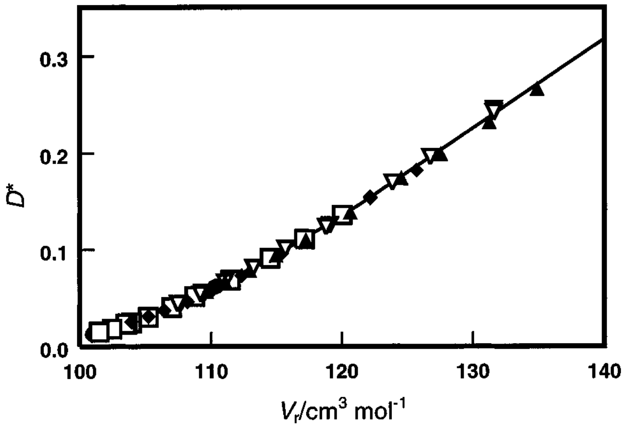

Figure 1. Reduced *self*-diffusion coefficients for hexane [(●) 223 K; (□) 248 K; (◆) 273 K; (▽) 298 K; (▲) 333 K], shifted to a common reference isotherm, 298 K (solid line).

$$D^*_{T2} = a_D \frac{D_{T2}}{(V)^{1/3}} \sqrt{\frac{\mu}{T}} \tag{5}$$

with $a_D = 17.44$ J$^{1/2}$ K$^{1/2}$ mol$^{2/3}$ when D_{T2}, V, μ, and T have units of 10^{-9} m^2/s, cm^3/mol, kg/mol, and K, respectively. Using these equations $D_{T2}(T,V)$ data can be fitted by nonlinear least squares yielding five parameters, ζ_i (i = 3) and ξ_j (j = 1, 2): eqs 1 and 4 can then be used to interpolate $D_{T2}(T,V)$ within the temperature and volume range of the original results. This approach has been used successfully for self-diffusion and viscosity data of a number of molecular liquids, including aromatic and aliphatic hydrocarbons (Harris, 1982, 1993; Harris *et al.*, 1993) and substituted methanes (Harris, 1993; Harris *et al.*, 1990). It has also formed a basis for the calculation of joint fits (Harris *et al.* 1993) for these two properties using a common V_{ref} function as well as the correlation of the transport properties for several series of related compounds through the construction of "family" curves from data for representative substances (Harris, 1993, 1995).

Results

The results of the fitting procedure for benzene and toluene in hexane using the data sets of Dymond (1981) and Dymond and Woolf (1982) are given in Table 1. A comparison of the results of Funazukuri *et al.* (1994) with values predicted by the correlations for these two systems is given in Table 2. Molar volumes were taken from the equation of state previously used for hexane (Harris, 1982). Generally, the difference between the data sets for the two systems is greater than the sum of the experimental errors.

A comparison has also been made between the Dymond−Woolf diaphragm-cell tracer diffusion results and the self-diffusion data for hexane referred to above, which were obtained by the nmr spin-echo technique. Within experimental error, the tracer diffusion coefficients have the *same* volume dependence as the self-diffusion coefficient, which is consistent with the lack of specific solute−solvent interactions in these systems. This result was obtained by fitting the tracer data to the equations (Harris, 1995)

$$D^*_{T2} = RD^*_{S1} \tag{6a}$$

$$V_{ref,T} = rV_{ref,S} \tag{6b}$$

where the subscripts T and S indicate tracer and self-diffusion, respectively. For benzene in hexane, $R = 1.13 \pm 0.02$ and $r = 0.999 \pm 0.002$, with a standard deviation of 3.5% and for benzene in toluene, $R = 1.08 \pm 0.03$ and $r = 0.999 \pm 0.003$, with a standard deviation of 3.6%.

Table 1. Coefficients of Eqs 1 and 4 for the Tracer Diffusion of Benzene and Toluene in Hexane (Diaphragm Cell Data)

	benzene + hexane	toluene + hexane
ζ_1	−1.677 06	−1.869 28
$10^2\zeta_2$/mol cm^{-3}	0.942 285	1.011 48
$10^{-2}\zeta_3$/cm^3 mol^{-1}	−0.434 897	−0.458 347
$10^3\xi_1$/K^{-1}	−0.767 240	−0.612 878
$10^5\xi_2$/K^{-2}	0.557 835	−0.652 308
T_{ref}/K	273.15	273.15
stand devn/%	2.5	3.1
expt acc/%	±2−4	±2−4

Table 2. Comparison of the Taylor Dispersion Results for the Tracer Diffusion of Benzene and Toluene in Hexane of Funazukuri *et al.* with the Correlation

T/K	p/MPa	V/cm^3 mol^{-1}	D/10^{-9} m^2 s^{-1}	D^*_{expt}	D^*_{calc}	$10^2(D^*_{expt} - D^*_{calc})/D^*_{expt}$
			benzene + hexane			
303.2	16	129.36	3.89	0.156	0.176	−12.7
313.2	16	130.97	4.48	0.176	0.191	−8.6
313.2	25	129.36	3.91	0.154	0.179	−16.2
323.2	16	132.65	4.86	0.187	0.206	−10.2
323.2	25	134.40	5.27	0.202	0.219	−8.6
			toluene + hexane			
303.2	16	129.36	3.79	0.158	0.169	−6.6
313.2	16	130.97	4.32	0.177	0.182	−2.9
313.2	25	129.36	3.82	0.157	0.170	−8.4
323.2	16	132.65	4.76	0.191	0.195	−2.0
323.2	25	134.40	5.24	0.209	0.208	0.6

This agreement between the volume dependence of the tracer and self-diffusion coefficients, obtained by different experimental techniques, allows one some confidence in the Dymond−Woolf tracer results. The systematic difference of the results of Funazukuri *et al.* may possibly be due to their use of a spectroscopic grade of hexane. Some manufacturers do not remove branched alkanes from this grade and the purity can be suprisingly low. For the benzene system, rather high concentrations were injected (10 to 50% by volume). Though the injected solution is considerably diluted in the Taylor technique, the result that the measured diffusion coefficients were independent of concentration under these conditions is suprising given the strong composition dependence of the mutual diffusion coefficient in this system at atmospheric pressure (Harris *et al.*, 1970). Whatever the reason for the differences between these particular data sets, the important point is that the method described here offers a general, direct way of making comparisons and analysis.

Nevertheless, this comparison would be fairer if more than one high-pressure isotherm were available for the reference data systems. At present, with this lack of data, (benzene + hexane) and (toluene + hexane) are not ideal for the calibration and cross-checking of the high-pressure Taylor dispersion diffusion apparatus, and alternatives are required.

The literature on high-pressure diffusion in liquids has been examined and the system (acetonitrile + methanol) is a better candidate for a calibration system. It has been more extensively studied by the high-pressure diaphragm-cell method than has (benzene + hexane) or (toluene + hexane), with data available for this system over the whole composition range and between 283 K and 313 K at pressures to 260 MPa (Hurle and Woolf, 1982b). Since acetonitrile and methanol self-diffusion data obtained with the same apparatus have been cross-checked against nmr spin-echo results (Hurle and Woolf, 1982a; Hurle *et al.*, 1985), one can have some confidence in these tracer results.

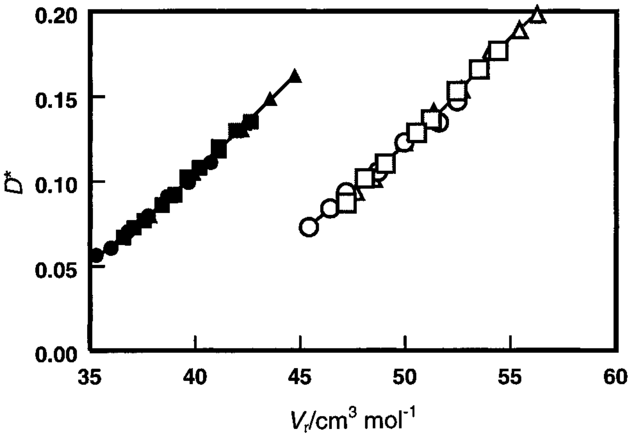

Figure 2. Reduced tracer diffusion coefficients for acetonitrile in methanol [(●) 283 K; (■) 298 K; (▲) 313 K] and methanol in acetonitrile [(○) 283 K; (□) 298 K; (△) 313 K] with $T_{\text{ref}} = 273.15$ K.

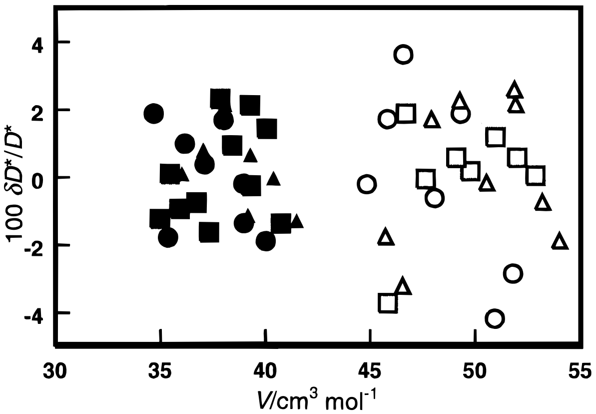

Figure 3. Deviation plot for acetonitrile in methanol [(●) 283 K;) 298 K; (▲) 313 K] and methanol in acetonitrile [(○) 283 K; (□) 298 K; (△) 313 K].

Table 3. Coefficients of Eqs1 and 4 for the System Methanol + Acetonitrile

	D_T(CH$_3$OH) in CH$_3$CN	D_T(CH$_3$CN) in CH$_3$OH
	−1.380 15	−0.989 654
$10\zeta_2$/mol cm^{-3}	0.186 377	0.174 065
$10^{-2}\zeta_3$/cm^3 mol^{-1}	−0.189 567	−0.145 398
$10^2\xi_1$/K^{-1}	−0.142 809	−0.175 025
$10^5\xi_2$/K^{-2}	0.882 390	−0.553 806
$_{\text{ref}}$/K	273.15	273.15
stand devn/%	2.4	1.5
expt acc/%	±2	±2

With suitable detectors, either the data set for D_T(acetonitrile) in methanol or that for D_T(methanol) in acetonitrile can be used for calibration and cross-checking. As both these substances show strong absorption only in the low ultraviolet, so that spectrophotometric detectors would have to be set on a band shoulder rather than a peak, the data are perhaps better suited to the calibration of bulk property detectors than to a uv spectrophotometer, unless the latter is very stable with respect to drift. Table 3 includes coefficients for eqs 1 and 4 for these two systems. The data are plotted in Figure 2 as reduced diffusion coefficients against reference molar volumes, and deviations from the fit are shown in Figure 3. The fit is satisfactory for both systems, though that for the diffusion of methanol in acetonitrile is the better of the two.

It should be noted that as the fitting is a nonlinear least squares procedure (adapted from Wentworth, 1965), one must be careful to avoid convergence on false minima on the multidimensional parameter-residual surface. This is dependent on using good initial estimates for the fitted parameters, though these can be found by trial and error with little difficulty. Experience with a variety of systems has shown that ζ_2 should be positive and ζ_3 negative and about a third to a half of the mean molar volume of the data set in magnitude. Fortran programs for fitting data are available from the author.

Table 4. Equations of State for Acetonitrile and Methanol

	CH$_3$CN	CH$_3$OH
$10^{-3}\alpha_{00}$/MPa	−1.251 65	−0.619 333
$10^{-6}\alpha_{01}$/MPa K	0.646 241	0.426 059
$10^{-1}\alpha_{10}$	0.437 740	0.229 812
$10^{-3}\alpha_{11}$/K	−0.121 637	0.110 283
$10^4\alpha_{20}$/(MPa)$^{-1}$	−79.929 8	−0.464 340
α_{21}/K (MPa)$^{-1}$	2.006 38	−0.812 999
std devn in κ/MPa	8.7	5.4
std devn in V/%[a]	0.1	0.06
β_0/cm^3 mol^{-1}	43.829 3[b]	32.579 5
$10^3\beta_1$/cm^3 mol^{-1} K^{-1}	−12.752 9	5.659 4
$10^5\beta_2$/cm^3 mol^{-1} K^{-2}	14.441 0	7.277 0
std devn/cm^3 mol^{-1}	0.006	

[a] Data for the fits were generated from smoothed functions for particular isotherms reported by Easteal and Woolf (1985a, 1985b) ($278 < T$/K < 323, $p < 280$ MPa), so the fit is better than would have been obtained from the raw experimental data. The advantage of the Hayward equation used is that it allows easy interpolation between experimental $p-V$ isotherms, as was required here. [b] Atmospheric pressure data for CH$_3$CN from Handa and Benson (1981), French (1987), and Sakurai (1992); β coefficients from Easteal and Woolf (1985b) for CH$_3$OH.

Appendix

Table 4 summarizes good quality literature pVT data for acetonitrile (Easteal and Woolf, 1985a) and methanol (Easteal and Woolf, 1985b) which can be used to obtain molar volumes. A Hayward equation of state is used, where the linear secant modulus

$$\kappa = V_\sigma(p - p_\sigma)/(V_\sigma - V) \tag{7}$$

is expressed as a polynomial in the pressure, p,

$$\kappa = \sum_{i=0}^{4} \alpha_i p^i \tag{8}$$

with temperature dependent coefficients

$$\alpha_i = \alpha_{0i} + \alpha_{1i}/T \tag{9}$$

V_σ is the liquid molar volume at atmospheric pressure or along the saturation curve. These V_σ values were fitted to a polynomial in the temperature,

$$V_\sigma = \sum_{i=0}^{2} \beta_i T^i \tag{10}$$

The coefficients α_{ij} and β_k are given in Table 4.

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