Use of a New Cell to Measure Diffusion Coefficients for the Systems Benzene–Carbon Tetrachloride and Sucrose–Water at 25°C

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Using a modified Tiselius cell, an Ingelstam Shearing diffusiometer has been used to measure the diffusion coefficients of the system benzene–carbon tetrachloride over the whole concentration range. These results are compared with new data and also with results previously obtained with the Gouy interference method. The new cell has also been tested with the system sucrose–water.

The aim of this paper is to report values of the diffusion coefficients over the whole concentration range for the binary liquid system benzene–carbon tetrachloride at 25°C, which were obtained with the birefringence interference and Gouy interference methods. From these results and from new results for the system sucrose–water, it is shown that the new cell employed in this study can be used to measure reasonable values for both aqueous and organic systems.

Experimental Method and Results

The shearing diffusiometer (*2, 8, 9, 12*) enables an image of a concentration gradient to be produced in the form of an interference pattern caused by the interaction between rays of plane-polarized light when passing through the gradient in a cell and then through a Savart plate. It can be shown (*12*) that the separation, 2 x, between any symmetrical pair of fringes changes with time according to the relationship:

$$(2x)^2 = [3A^2t^2/(3At - b_1^2)][1 + \ln(B/t)] - [b_1^2At/(3At - b_1^2)] \quad (1)$$

where $A = 8\ D$ (D = diffusion coefficient), B = time of maximum separation of a fringe pair, and b_1 is a quantity related to the shear distance, b, of the Savart plate by $b_1 = (b/G)$, where G is an optical magnification factor. The parameters A and B are obtained by a nonlinear least-squares fit (*12*) of Equation 1 to the experimental data. The best values of A and B are obtained when an additional zero-time correction, Δt, is calculated which minimizes the standard deviation of the points from the curve. This correction allows for the finite width of the boundary at zero time.

The Gouy interference method is well known and has been described in detail elsewhere (*4, 5, 10, 11*).

The cell used in these experiments is shown in Figure 1. It differs from the two-slit greased cell described in ref. *12* in that it is a complete unit with no movable parts. It is an improved version of the prototype cell, described by Harris et al. (*7*), which is a complete unit but which has no outlet slits at the level of the optic axis and which requires the use of the capillary siphoning technique in forming the diffusion boundary. Instead of having the reservoir section slide across until it is open to the diffusion channel, this cell uses two holes (whereas the cell described in ref. *7* has only one hole) into which one can insert teflon plugs, fixed to the ends of brass rods. Thus the need for grease is eliminated and the cell is suitable for use with organic systems. To perform an experiment, the denser solution is introduced into the cell up to the level of the two holes, and the plugs are inserted on the side of the cell through which the monochromatic light beam passes. The reservoir above the plugs is rinsed with the less dense solution and then filled with the same solution. The reservoir on the other arm of the cell is then filled approximately to the same level with the denser solution. (For significant differences in density between the two solutions, the heads must be adjusted for hydrostatic stability.) After thermal equilibrium is reached, the teflon plugs are removed and a rough boundary formed. The solutions in the cell are then siphoned out through a single 0.05-mm slit at the level of the optic axis. When the rough boundary reaches this level it is immediately sharpened. A diffusion experiment is commenced by terminating the siphoning.

All experiments were carried out in a thermostat bath filled with deionized water. The bath temperature was maintained at 25.000° ± 0.002°C with a mercury-toluene regulator and a thyratron relay. Benzene and carbon tetrachloride were purified by fractional distillation and the purities, determined by gas-phase chromatography, were found to be better than 99.99%. The water used in the aqueous runs was first deionized and then distilled. The sucrose was a standard sample supplied by the National Bureau of Standards and was used without further purification. All solutions were prepared gravimetrically, the weights being corrected to vacuo.

Diffusion data for the system carbon tetrachloride–benzene obtained with the shearing diffusiometer is given

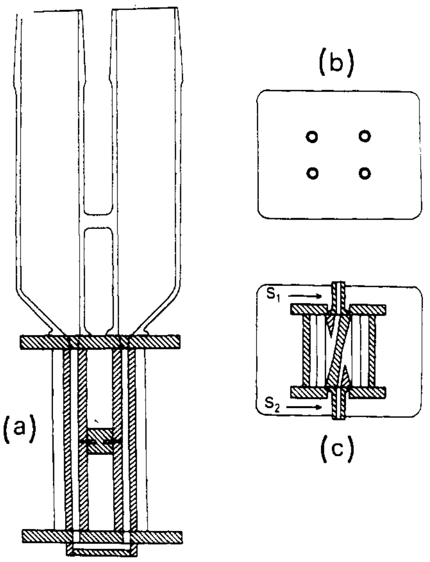

Figure 1. Modified fixed-section Tiselius-type cell
(*a*) side view; (*b*) section at the level of the holes; (*c*) section at the level of the optic axis; S_1 and S_2 are siphoning outlets leading from respective slits.

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Table I. Diffusion Data for CCl_4-C_6H_6 at 25°C Using the Shearing Diffusiometer

Run	N_{CCl_4}[a]	ΔN_{CCl_4}[b]	$(2x)_{max} \times 10^2$, meters	t_{max}, sec	Δt, sec	$D \times 10^9$, meters^2 sec^{-1}
35A	0.006545	0.01309	0.4627	901.0	5.0	1.979
B			0.4598	895.8	6.8	1.965
37A	0.500096	0.011297	0.4181	890.1	6.9	1.636
B			0.4181	877.0	4.3	1.637
C			0.4111	867.4	3.2	1.618
36A	0.99472	0.01054	0.3898	853.6	4.3	1.484
B			0.3892	846.8	(−1.8)[c]	1.490
C			0.3859	861.0	10.2	1.441

[a] Mean mole fraction of CCl_4 across the boundary. [b] Mole fraction difference of CCl_4 across the boundary. [c] If the robot camera (see ref. *12*) was not started at the same instant as siphoning was terminated, a negative value of Δt could be obtained.

in Table I. This is compared with similar Gouy data determined in previous work (*3*). The latter data are listed in Table II together with one Gouy run carried out with the new cell in the present study. Both sets of data are summarized on the graph in Figure 2. Data from shearing diffusiometer runs for sucrose in water are listed in Table III.

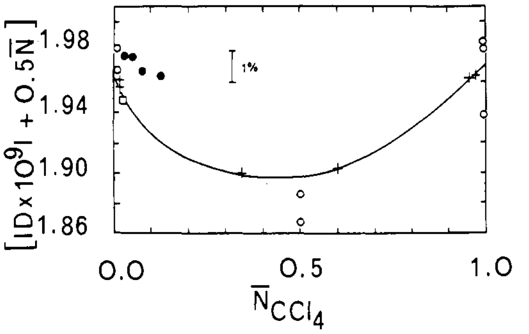

Figure 2. Composition dependence of the diffusion coefficient of the system carbon tetrachloride-benzene

○, this work, Shearing diffusiometer; □ this work, Gouy diffusiometer; +, Dunlop, Gouy diffusiometer (*3*); ● Hammond and Stokes, diaphragm cell (*6*); units of D are meters^2 sec^{-1}

Table II. Diffusion Data for CCl_4-C_6H_6 at 25°C Using the Gouy Diffusiometer

$\bar{N}_{CCl_4}$	ΔN_{CCl_4}	No. of fringes, J	$D \times 10^9$, meters^2 sec^{-1}
0.01647	0.03294	75.27	1.952
0.01847	0.03694	85.38	1.948
0.02265[a]	0.04530	114.75	1.937
0.3442	0.04564	89.09	1.737
0.6018	0.05522	108.64	1.602
0.9580	0.0840	163.20	1.485
0.9760	0.04786	93.33	1.476

[a] New cell used.

Discussion

Agreement between Gouy and shearing diffusiometer results for the carbon tetrachloride-benzene system is quite good, as Figure 2 indicates. The estimated errors in the diffusion coefficients from the two methods are ±0.1% and ±0.3%, respectively. Since the Gouy method is inherently more precise than the birefringence method, the curve in Figure 2 is taken as a qualitative best fit through the points corresponding to the Gouy results. The results of the two methods agree to about 1%. In addition, Hammond and Stokes diaphragm cell data (*6*) for this system are fairly consistent with our results. They obtained diffusion coefficients toward the benzene end of the concentration range.

Since benzene and carbon tetrachloride are volatile liquids, a special precaution was taken to prevent changes in concentration of the mixture due to evaporation. This was achieved by saturating the space above the mixture with vapor at atmospheric pressure from the same mixture in another vessel, connected to the cell by plastic tubing.

For the aqueous system sucrose-water (Table III), the diffusion data obtained with the greased cell and the fixed-section cell agree favorably and this shows that one outlet slit at the optic axis is sufficient to form a sharp diffusion boundary. Since the birefringence method is sensitive to small changes in refractive index, very dilute solutions and hence very small concentration differences are used. Gouy data at 25°C for this system in the literature (*1*) extrapolate to 0.5228×10^{-9} meter^2 sec^{-1} at infinite dilution, and Bryngdahl (*2*) obtained a value of 0.5229×10^{-9} meter^2 sec^{-1} at a mean concentration of 0.00033*M* with the Shearing diffusiometer. Pepela et al. (*12*) obtained a value of 0.525×10^{-9} meter^2 sec^{-1} at a mean concentration of 0.00262*M*, which is essentially in perfect agreement with our results. Harris et al. (*7*) tested their prototype fixed-section diffusion cell on this system using the Gouy interference method. In general, they found their results to agree within 0.3% of the values calculated from the data of Akeley and Gosting (*1*).

Table III. Diffusion Data for Sucrose-Water at 25°C Using the Shearing Diffusiometer

Run	$\bar{C}_{sucrose}$,[a] mol dm^{-3}	$\Delta C_{sucrose}$,[b] mol dm^{-3}	$(2x)_{max} \times 10^2$, meter	t_{max}, sec	Δt, sec	$D \times 10^9$, meter^2 sec^{-1}
40[c]	0.00247	0.00493	0.2188	759.0	8.0	0.525_4
41A	0.00247	0.00494	0.2275	820.8	12.9	0.525_4
B			0.2267	818.2	15.1	0.523_2
C			0.2273	817.7	12.7	0.526_3

[a] Mean concn (mol dm^{-3}) of sucrose across the boundary. [b] Concn difference of sucrose across boundary. [c] Greased cell was used.

Whereas the boundary formation process used by Harris et al. was adequate for large concentration gradients (as in the Gouy method), a sharp boundary could not be formed in this way for small concentration gradients (as in the birefringence method), and this led to the design of the present cell. Its advantages are, as this study has shown, first the ability to work with both aqueous and organic systems, and second the ability to form sharp boundaries with small- and large-concentration gradients.

In addition, the larger reservoirs, coupled with two holes instead of one, enable a more efficient washing of the region above the boundary than the prototype used by Harris et al. (7).

Only one Gouy run has been carried out for the system benzene-carbon tetrachloride with the new cell, but it is believed that this cell will be used to its full potential if a concentration dependence study for a number of organic systems is done using Gouy and birefringence methods.

Literature Cited

(1) Akeley, D. F., Gosting, L. J., *J. Amer. Chem. Soc.*, **75**, 5685 (1953).
(2) Bryngdahl, O., *Acta Chem. Scand.*, **11**, 1017 (1957).
(3) Dunlop, P. J., unpublished data, 1972.
(4) Gosting, L. J., Morris, M. S., *J. Amer. Chem. Soc.*, **71**, 1998 (1949).
(5) Gosting, L. J., Onsager, L., *ibid.*, **74**, 6066 (1952).
(6) Hammond, B. R., Stokes, R. H., *Trans. Faraday Soc.*, **51**, 1641 (1955).
(7) Harris, K. R., Pua, C. K. N., Dunlop, P. J., *J. Phys. Chem.*, **74**, 3518 (1970).
(8) Ingelstam, E., *Ark. Fys.* **9**, 197 (1955).
(9) Ingelstam, E., *J. Opt. Soc. Amer.* **47**, 536 (1957).
(10) Kegeles, G., Gosting, L. J., *J. Amer. Chem. Soc.*, **69**, 2516 (1947).
(11) Longsworth, L. G., *ibid.*, **69**, 2510 (1947).
(12) Pepela, C. N., Steel, B. J., Dunlop, P. J., *ibid.*, **92**, 6743 (1970).

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Excess Enthalpies, Volumes, and Surface Tensions of Isomeric Butanol-*n*-decanol Mixtures

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Enthalpies of mixing, volumes of mixing, and surface tensions were measured for the three binary systems: isobutanol–*n*-decanol, *sec*-butanol–*n*-decanol, and *tert*-butanol–*n*-decanol. All determinations were carried out at 25°C, except for the calorimetric measurements on the system *tert*-butanol–*n*-decanol, which were made at 26°C. Correlation of the results by the theory of Flory combined with the principle of corresponding states was investigated.

Previous publications *(1, 8, 10)* from our laboratory have described investigations of the excess properties of the system *n*-butanol–*n*-decanol. These studies have been extended by measuring the excess enthalpies, excess volumes, and surface tensions of the binary systems formed by mixing isobutanol, *sec*-butanol, and *tert*-butanol with *n*-decanol.

Experimental

Isobutanol (2-methyl-1-propanol), *sec*-butanol (2-butanol), *tert*-butanol (2-methyl-2-propanol), and *n*-decanol were purified chromatographically *(9, 10)*. The purity of all samples used for the mixtures exceeded 99.8%.

Details of the experimental apparatus and procedures have been described previously *(5, 6, 8, 10)*. Except where indicated otherwise, all measurements were made at 25.00° ± 0.01°C.

Excess enthalpies for the systems isobutanol–*n*-decanol and *sec*-butanol–*n*-decanol were determined in the successive dilution calorimeter of Pope et al. *(10)*. The modified form of that calorimeter *(6)* (containing a cooling module) was used to study the system *tert*-butanol–*n*-decanol, and the measurements were made at 26.00° ± 0.01°C since it was difficult to operate the calorimeter at 25°C with *tert*-butanol as a supercooled liquid *(9)*. The error of the calorimetric measurements is believed to be less than 1%.

Volumes of mixing were measured directly in a dilatometer *(8)* using a successive dilution technique. The overall errors of the results for equimolar mixtures are estimated to be about 1%.

Surface tensions of the pure liquids and of their binary mixtures were determined by the maximum bubble pressure method *(5)*. The bubbler was calibrated frequently with research grade benzene (Phillips Petroleum Co.), assuming a surface tension of 28.20 dyn cm^{-1} for that material at 25°C. Values of the surface tension were generally reproducible within ±0.03 dyn cm^{-1}.

Results and Discussion

The experimental results for the molar excess enthalpy and molar excess volume are listed in Tables I and II. For each system, x_1 denotes the mole fraction of the butanol isomer. The observed surface tensions, along with values of the excess surface tension defined by the equation

$$\gamma^E = \gamma - x_1\gamma_1 - x_2\gamma_2 \qquad (1)$$

are summarized in Table III.

The method of least squares was used to fit the results for each of the excess functions with an equation of the form

$$X^E = x_1x_2 \sum_{j=1}^{n} c_j(x_2 - x_1)^{j-1} \qquad (2)$$

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