Temperature and Concentration Dependence of Diffusion Coefficient in Benzene-*n*-Heptane Mixtures

Waclaw F. Calus[1] **and Myo T. Tyn**[2]
Department of Chemical Engineering, Loughborough University of Technology, Leicestershire, England

The two-compartment diffusion cell reported by Stokes was modified for operation at temperatures higher than the ambient temperature. Experimental diffusion coefficients were obtained for concentrations of 0.05, 0.25, 0.50, 0.70, and 0.96 mole fraction of benzene in *n*-heptane at 25°, 45°, 65°, 75°, and 85°C. Diffusion coefficients at normal boiling points of these mixtures were obtained by extrapolation and interpolation. Also, the diffusion coefficients at infinite dilution for benzene and *n*-heptane were obtained by extrapolation at all the temperatures of the experiment.

The design of engineering process equipment requires a knowledge of physical and transport properties at elevated temperatures, usually at boiling points in such operations as distillation and boiling. The diffusion coefficient in binary and multicomponent mixtures is one such property often recorded in the literature for ambient temperatures only. The existing theoretical or semiempirical equations for the prediction of diffusion coefficients as a function of temperature or concentration are not reliable since they are based only on a partial knowledge of the mechanism of diffusion in liquids. Even to use these equations for extrapolation of the experimental data to higher temperatures or to other concentrations could lead to serious errors, at least in the case of some groups of chemical compounds.

The object of this work is to obtain experimentally some values of the diffusion coefficient for a series of mixtures of benzene with *n*-heptane at a range of temperatures up to the atmospheric boiling point.

Koeller and Drickamer (*3*) used a small diffusion cell in a pressure bomb in their investigation of the effect of pressure on the diffusion coefficient. In our investigation low pressures had to be used, not higher than that just necessary to suppress boiling; therefore, it was found more practicable to adapt the well-proved Stokes' (*6*) two-compartment cell.

Experimental

A two-compartment cell with a diaphragm in a horizontal position as described by Stokes (*6*) was adapted for the operation at temperatures higher than the ambient. The operation at higher temperatures introduces two additional factors complicating the performance of the apparatus—expansion of the test liquids and evaporation or even boiling. If no provision was made for expansion, a bulk flow through the diaphragm would occur in a cell (*6*). Evaporation of the test liquids would alter the concentrations, and boiling would alter the concentrations and cause vapor locking of some of the channels in the porous diaphragm.

The cell finally developed and used is shown in Figure 1. The feed tube D of the lower compartment, in which the heavier liquid is accommodated, ends with an expansion E of approximately the same volume and shape as the top of the upper compartment above the dotted line C. The heavier test liquid introduced at ambient temperature has its level at the mouth of the capillary; the lighter liquid has a slightly higher level in the upper cell. On thermal expansion the heavier liquid partly fills the expansion E, and the lighter liquid expands in its own compartment above the dotted line C.

To prevent boiling, advantage is taken of the observation made by Doane and Drickamer (*1*) that minor changes in the total pressure on the system have no significant effect on the magnitude of the diffusion coefficient. In this investigation a maximum pressure of 20 psig was used. The effect of pressure on the diffusion coefficient was investigated (*1*), and it appears that a rise of 20 psi in the pressure could lower the coefficient by approximately 0.2%. The pressure on the cell is applied by connecting the cells to a nitrogen gas cylinder through a pressure reducing valve. To insure equal pressure on both compartments, the connecting tubes F are of the same diameter and of the same length. This precaution is necessary in case a small gas leak exists on the joints.

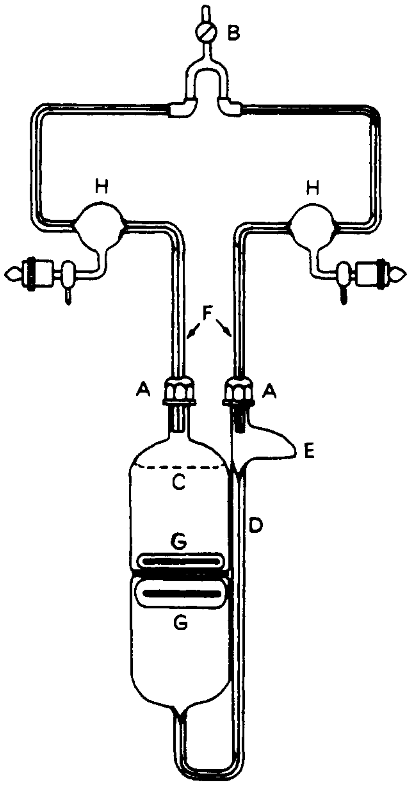

Figure 1. Diffusion cell
A Gas tight joints
B Nitrogen supply control valve
C Liquid level in upper compartment
D Capillary tube to expansion space of lower compartment
E Expansion space of lower compartment
F Capillary tubes connecting cell to nitrogen supply
G Magnetic stirrers
H Condensate trap

---

[1] To whom correspondence should be addressed.

[2] Present address, Foodstuffs Corp., Rangoon, Burma.

In the course of these experiments no condensation was noticed on the tubes F, and the condensate traps H were never used. In the original Stokes apparatus the tube D had a substantial cross section. In this apparatus a small bore capillary approximately 1½-mm diameter was used to reduce the volume of the stagnant liquid. Also, the connecting tubing was made of small bore capillary to reduce the volumetric hold up of the gas phase, and thus, to reduce the experimental error owing to evaporation of the test liquids.

The volume of the lower compartment is approximately equal to that of the upper compartment below the line C, each of 65 cm^3. The volume of the pores in the diaphragm is 0.30 cm^3. The ratio of the volumes, λ = 0.0046, is considerably below the acceptable maximum (*5, 6*). The diaphragm is a sintered glass disc manufactured by Jencons Scientific Limited, 4 cm in diameter, porosity number 4, and pore size 5–10 μ.

The stirrers are made of glass tubes with soft iron wires sealed in them. The upper stirrer is heavy enough to rest on the diaphragm, and the lower one light enough to float on the top of the heavier liquid in the lower compartment. During the development runs it was decided to wrap the stirrers with a thin PTFE sheet to avoid attrition of the diaphragm. The stirrers were operated with a pair of magnets fixed to a rotating U-shaped yoke. The cell, together with the rotating magnets, was immersed in a bridge-controlled thermostat bath using a high boiling-point oil. A constant temperature was maintained with an accuracy of ±0.1°C.

The insertion of the test liquids and the pressurizing of the cell were done outside the hot bath at the ambient temperature. Then the cell was immersed in the oil bath, which was brought to the appropriate temperature beforehand, and the stirrers were started up. In the first 5 min approximately the expansion of the liquid was completed, which meant that the test liquid attained the temperature of the bath. During that period adjustments to the pressure on the system were made if necessary. During that preheating period the rate of diffusion owing to the increasing temperature was not constant; this is one of the causes of the existence of an experimental error.

The stirrers' speed throughout this work was maintained at 37 rpm, and the duration of each experiment was 24 hr. At the end of this period the stirrers were stopped, and the cell was pulled out of the bath and cooled down first in the stream of air and finally in a bath of cold water. After the ambient temperature was reached, the cell was depressurized, and the test liquids were removed for an analysis.

Throughout the experimental work the concentration ratio in the two compartments $(C_1 - C_2)/(C_3 - C_4)$ was maintained at approximately 1.6 which is considerably above the minimum of 1.2 (*4*). The cell constant β was

Table I. Experimental Results of This Work and of Trevoy and Drickamer (8)

Run no. or ref	Benzene concn mole fraction	Temp, °C	$D_{AB} \times 10^5$, cm^2/sec	Press on cell, psig	Cell constant β	% Dev from straight line, Figure 4	% Dev from straight line, Figure 3
1	0.0465	24.5	3.26	0	0.1299	0	+2.3
2	0.0475	44.5	4.19	0	0.1305	−0.7	−2.3
3[a]	0.0475				0.1310		
4	0.0505	64.5	5.83	2	0.1314	0	+2.2
5	0.0485	75.0	6.37	5	0.1320	−1.2	−0.4
6	0.0475	85.0	7.12	5	0.1326	−0.8	−0.2
7	0.2460	25.0	2.292	0	0.1338	0	+0.7
8[a]	0.2385				0.1344		
9	0.2395	65.0	5.25	5	0.1350	0	+2.2
10	0.2385	75.0	5.83	5	0.1356	0	+0.7
11	0.2280	85.0	6.45	7	0.1361	−1.4	0
12	0.2560	25.0	2.90	0	0.1374	0	0
13	0.2550	45.0	3.65	1	0.1380	−3.6	−6.3
14	0.2535	65.0	5.22	7	0.1386	+0.7	+1.7
15	0.2545	75.0	5.85	10	0.1391	+1.1	+0.9
16	0.2540	85.0	6.52	10	0.1398	+1.4	−0.3
17	0.5050	25.0	2.77	0	0.1410	+8.7	+7.6
Ref 8	0.5000	25.0	2.47	0		−3.2	−4.3
18	0.5050	45.0	3.47	5	0.1416	+4.2	−0.5
Ref 8	0.5000	45.0	3.40	0		+2.0	−2.0
19	0.5035	65.0	4.28	8	0.1422	−4.6	−5.7
Ref 8	0.5000	65.0	4.31	0		−4.0	−5.1
20	0.5050	75.0	5.15	10	0.1428	+1.3	+0.5
21	0.5050	83.2	5.75	12	0.1433	+1.6	+0.4
22	0.7030	25.0	2.10	0	0.1444	−8.4	−4.1
23	0.7010	45.0	2.93	3	0.1452	−2.1	−0.1
24	0.7010	65.0	3.84	10	0.1457	−3.9	0
25	0.7010	75.0	4.53	13	0.1463	−0.8	+4.3
26	0.7010	85.0	4.89	20	0.1469	−3.9	0
27	0.9605	25.0	2.07	0	0.1471	+3.9	+2.9
28[a]	0.9605						
29	0.9605	45.0	2.68	3	0.1491	+2.8	−1.8
30	0.9605	65.0	3.64	13	0.1499	+6.0	+2.2
31	0.9605	75.0	4.00	17	0.1505	+0.6	0
32	0.9605	85.0	4.56	20	0.1511	+3.0	+0.1

[a] Spoiled runs.

calculated from the relationship for the integral diffusion coefficient (*2*):

$$D_{AB} = \frac{1}{\beta t} \log \frac{C_1 - C_2}{C_3 - C_4} \qquad (1)$$

The value of the constant β increased from 0.1299 to 0.1511, i.e., by 16.3% in the working time of 960 hr. The same cell was used for the whole experimental program described in this report. The calibration of the cell was done with 0.1*N* KCl solution and distilled water. The value of the integral diffusion coefficient for this system, D_{AB} = 1.87 × 10^{-5} cm^2/sec, was taken from Stokes (*6*). The analysis of KCl–H_2O solutions was carried out in accordance with the recommendations of Vogel (*10*). The value of the constant β was determined after every 140 hr of running time. A plot of β against the time gave a straight line with a scatter of points within ±0.7% accuracy lines. Therefore, for the calculation of each coefficient from the run data, the appropriate value of the constant β was taken from this plot.

Reagent-grade benzene and *n*-heptane were used to prepare the test solutions for the diffusion coefficient determinations. The analysis of the benzene–*n*-heptane mixtures was done by means of the Hilger and Watt refractometer, permitting readings of the refractive index to four decimal places. A refractive index calibration chart for this system was prepared and agreed closely with that published by Timmermans (*7*). Each test liquid was analyzed three times, and the mean was recorded.

The overall experimental error is made up of the following components: errors in the concentration measurements, a somewhat smaller rate of diffusion in the preheating period lasting about 5 min, some losses of the lighter component to the gas phase during the experiment, and the effect of pressure on the diffusion coefficient. It has been estimated that the overall accuracy of these results is well within the ±2% accuracy limits. The experiments to assess the reproducibility of the experimental results gave a maximum deviation of 0.75%.

Results

Diffusion coefficients for the system benzene–*n*-heptane were measured for the following nominal concentrations: 0.05, 0.25, 0.50, 0.70, and 0.96 mole fraction benzene at temperatures of 25°, 45°, 75°, and 85°C. The integral coefficients D_{AB} were calculated from Equation 1 and the experimental data obtained in the diffusion cell described in the previous section. Table I gives a record of the experimental conditions and the results, together with some values of the coefficient obtained by Trevoy and Drickamer (*8*). Most of the experimental points are the result of a single determination. Runs 12–16, for the nominal concentration of 0.25 mole fraction, were duplicates of runs 7–11. Ignoring the small difference in the actual concentrations of the two sets of runs, the deviation for each pair does not exceed 0.75%, which is far below the estimated overall experimental error of ±2%.

The experimental data of Trevoy and Drickamer (*8*) are compared with the appropriate experimental data points of this work in Table II, and on the whole, the agreement is good. Since the data of Trevoy and Drickamer (*8*) were obtained by a different method (a cell with a vertical diaphragm and without mixing), it is thought that our data can be treated as reliable.

Our experimental data and those of Trevoy and Drickamer are shown in Figure 2 as plots of D_{AB} against concentration with temperature as a parameter. Also in Figure 2 each isotherm is extrapolated to a concentration of benzene X_A = 0 and X_A = 1, and the values of the diffusion coefficients at infinite dilution are obtained and recorded in Table III. It is suggested that the accuracy of these coefficients by extrapolation is about the same as that of the experimental points, i.e., ±2%, since the extrapolation distance is small, and the curve D_{AB} vs. X_A is not too different from straight lines.

Diffusion coefficients at boiling points for the mixtures 0.05, 0.25, 0.50, 0.70, and 0.96 mole fraction benzene were obtained by extrapolation and interpolation of the experimental data in Figure 3. The basis of the procedure adopted in Figure 3 is the conclusion from the Eyring theory (*5*) that the plot of ln D_{AB} against the reciprocal of the absolute temperature gives a straight line if it is assumed that the effect of temperature on the term containing the partition function, in Equation 8 of Smith and Storrow (*5*), is small and can be ignored.

Inspection of Figure 3 shows that the best lines through the data points for each concentration are parallel, and the scatter of the experimental data around the respective curves is small. The deviation of each point

Table II. Experimental Coefficients of This Work and of Trevoy and Drickamer (*8*) Compared, $D_{AB} \times 10^5$ cm^2/sec

Benzene mole fraction	Temp, °C	Exptl D_{AB}, this work	Exptl D_{AB}, ref. *8*	% Deviation
0.5	25	2.77	2.47	−10.8
0.5	45	3.47	3.40	−2.0
0.5	65	4.28	4.31	+0.7

Table III. Diffusion Coefficients at Infinite Dilution, $D_{AB}°$ and $D_{BA}° \times 10^5$ cm^2/sec (Obtained from Figure 2 by Extrapolation)

Temp, °C	$D_{AB}°$ benzene in *n*-heptane	$D_{BA}°$ *n*-heptane in benzene
25	3.40	2.10
45	4.40	2.75
65	6.05	3.65
75	6.55	4.07
80.1		4.25
85	7.30	4.60
98.4	8.40	

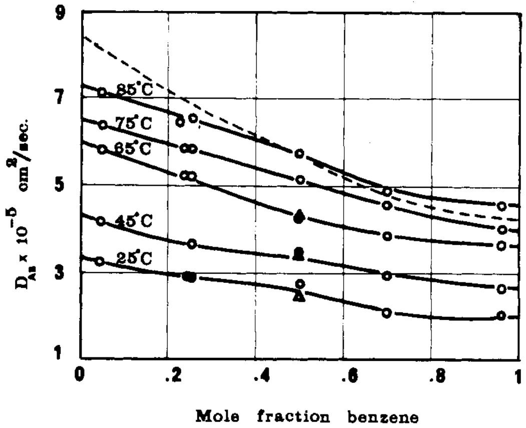

Figure 2. Experimental diffusion coefficients of this work and of Trevoy and Drickamer (*8*) for benzene and *n*-heptane mixtures

○ This work

△ Trevoy and Drickamer (*8*)

---- Diffusion coefficient at normal boiling point

Numbers on lines indicate temperature in °C from its line is shown in the last column of Table I; at the temperature of 85°C—very close to the boiling points of the various solutions—the maximum deviation is only 0.4%. Therefore, it is assumed that the accuracy of the diffusion coefficients at the boiling points from Figure 3 is essentially the same as that of the experimental data points—±2%. These coefficients are shown in Table IV.

Table IV. Diffusion Coefficients at Normal Boiling Points, by Extrapolation or Interpolation in Figure 3, $D_{AB} \times 10^5$ cm²/sec

Benzene mole fraction	Bp, °C	Experimental coefficient of this work, from Figure 3 D_{AB}
0.05	96.4	8.10
0.25	90.3	6.82
0.50	85.0	5.78
0.70	82.2	4.68
0.96	80.2	4.27

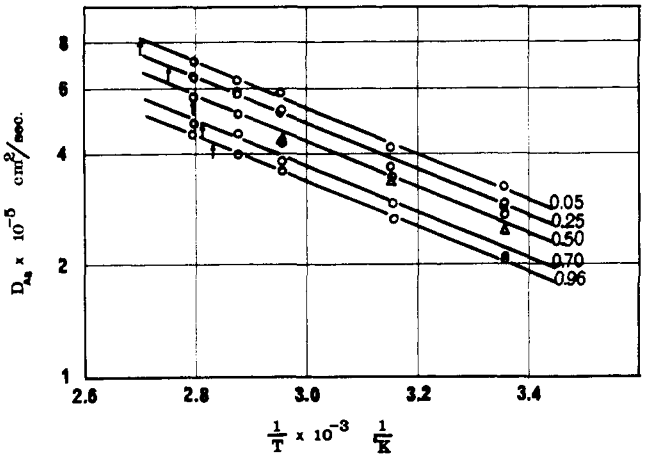

Figure 3. Variation of diffusion coefficient with reciprocal of absolute temperature
O This work
Δ Trevoy and Drickamer (8)
† Indicates boiling point of mixture
Numbers on lines indicate concentration of benzene, mole fraction

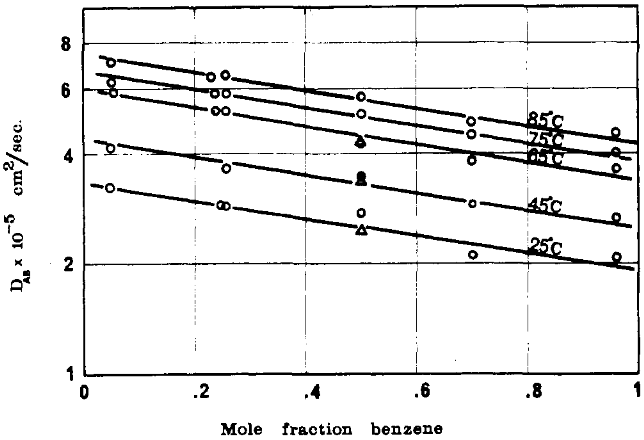

Figure 4. Variation of D_{AB} with concentration for mixtures of benzene with *n*-heptane
O This work
Δ Trevoy and Drickamer (8)
Numbers on lines indicate temperature in °C

Discussion

Experimental values of diffusion coefficients at all the concentrations and temperatures are recorded in Table I. According to Vignes (9) for near-ideal solutions, in which the benzene-*n*-heptane system is here included, a plot of diffusion coefficients against the concentration isotherm should give a curve concave upward lying below the straight line joining the extremities of the curve. Figure 2 does not entirely verify this statement—the equimolal mixture is responsible for spoiling this pattern.

Diffusion coefficients at infinite dilution, obtained by extrapolation to zero concentration of benzene and zero concentration of *n*-heptane, are shown in Table III. A plot of the experimental coefficients against mole fraction concentration in Figure 2 was used for this purpose. The plot of ln D_{AB} against mole fraction in Figure 4, which according to Vignes (9) should give a straight line for near-ideal solutions, gives reasonable agreement with the extrapolations done in Figure 2. However, these coefficients deviate from the best straight lines in Figure 4 within the accuracy limits of −8.4% and +8.7%, as shown in Table I.

Diffusion coefficients at normal boiling point were obtained by extrapolation or interpolation procedures based on the Eyring theory. The procedure is shown in Figure 3, and the resulting coefficients are tabulated in Table IV.

It has already been suggested that the accuracy of the experimental coefficients is well within the ±2% accuracy limits. In view of a very short extrapolation distance in estimating the diffusion coefficients at infinite dilution and those at the normal boiling points, it is suggested that similar accuracy limits of ±2% should be assigned to them also.

Nomenclature

C_1 = initial concentration in the lower compartment, mole fraction
C_2 = initial concentration in the upper compartment, mole fraction
C_3 = final concentration in the lower compartment, mole fraction
C_4 = final concentration in the upper compartment, mole fraction
D_{AB} = integral diffusion coefficient, cm²/sec
D_{AB}° = diffusion coefficient at infinite dilution, cm²/sec
t = time, sec
T = temperature, K
β = cell constant in Equation 1
λ = the ratio of pore volume in the diaphragm to the volume of the cell compartment
X = concentration, mole fraction

Subscripts

A = benzene
B = *n*-heptane

Literature Cited

(1) Doane, E. P., Drickamer, H. G., *J. Chem. Phys.*, **21**, 1359 (1953).
(2) Holmes, J. T., *Rev. Sci. Instrum.*, **36**, 831 (1965).
(3) Koeller, R. C., Drickamer, H. G., *J. Chem. Phys.*, **21**, 267 (1953).
(4) Sarram, P., MSc thesis, Loughborough University of Technology, Leicestershire, England, 1969.
(5) Smith, I. E., Storrow, J. A., *J. Appl. Chem.*, **2**, 225 (1952).
(6) Stokes, R. H., *J. Amer. Chem. Soc.*, **72**, 763 (1950).
(7) Timmermans, J., "Physico-Chemical Constants of Binary Mixtures," Vol 1, p 74, Interscience, New York, N.Y., 1960.
(8) Trevoy, D. J., Drickamer, H. G., *J. Chem. Phys.*, **17**, 1117 (1949).
(9) Vignes, A., *Ind. Eng. Chem. Fundam.*, **5**, 189 (1966).
(10) Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis," 3rd ed., p 259, Longmans, 1962.

Received for review September 5, 1972. Accepted April 14, 1973.