Liquid Diffusivities for the System *n*-Propanol–Toluene

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Measurements of the liquid diffusivities over the complete range of compositions of the *n*-propanol–toluene system at atmospheric pressure and 25° C. have been carried out using the magnetically-stirred porous diaphragm cell technique. Diffusivities calculated on the usual basis of concentration as driving force have a minimum at about 0.5 mole fraction *n*-propanol. There is a four-fold variation of diffusivity over the entire composition range, and general behavior is similar to analogous nonideal systems. At infinite dilution none of the semi-empirical correlations, based on various models of the liquid state, give values in agreement with experiment.

DIFFUSION in liquid systems has both theoretical and practical importance. Accurate experimental liquid diffusivities (diffusion coefficients) are essential for checking various theories of the liquid state, as well as for studies on mechanisms of mass transfer. Considerable interest attaches to nonideal multicomponent systems in this regard.

As part of a continuing program (*2, 12*) to meet in some measure, this need for such data, the binary system *n*-propanol-toluene was selected for investigation. No diffusion data have been reported previously on this system.

EXPERIMENTAL METHOD

The diaphragm cell technique as modified by Dullien and Shemilt (*2*) was employed with some further minor improvements discussed elsewhere (*12*). In such a cell the integral diffusivity, $\bar{D}$, can be determined using the integrated form of Fick's (*5*) first law of diffusion:

$$\bar{D} = \frac{1}{\beta\theta} \ln \frac{\Delta C_o}{\Delta C_f} \tag{1}$$

The assumptions involved in the derivation of Equation 1 and the conditions under which they hold are dealt with in detail by Gordon (*6*). These are essentially the achievement of quasisteady state in the diaphragm, the constancy of cell constant β, negligible volume changes on mixing, the homogeneity of solutions in both compartments, and nonexistence of surface transport or streaming in the diaphragm. In the present investigation, the required conditions could be met (*16*), which made possible the use of Equation 1. If hydrodynamic velocity—i.e., bulk transfer due to volume changes or mixing, cannot be neglected, then considerably more complex relationships must be used (*3, 13*).

The potassium chloride, used for determination of cell constant β, was Baker Analyzed reagent grade. Fisher certified reagent grade *n*-propanol was treated with pure calcium oxide to neutralize residual acids and subsequently with silica gel to remove any traces of water. Fisher certified reagent grade toluene was similarly treated with silica gel. Both *n*-propanol and toluene were then distilled separately in a Todd precision fractionation column operated at 20 to 1 reflux ratio. Gas chromatographic analysis before and after distillation indicated that the impurities were reduced to less than 1 part in 10,000. The distilled liquids were stored and handled under drybox conditions.

The procedure in the diaphragm cell technique involved three steps: cell constant determination, establishment of pseudo-steady-state conditions in the diaphragm, and the actual diffusion run.

Cell constants β were determined using aqueous potassium chloride solutions for which accurate diffusivity data have been given by Stokes (*18*). This widely accepted procedure is based on the justifiable assumption (*6*) that volume changes on mixing that occur with the dilute potassium chloride solution may be neglected. The establishment of pseudo-steady-state in the diaphragm required careful filling of the two cell compartments with solutions of differing composition and allowing the diffusion to take place for 2 to 3 hours. The solutions were then replaced by fresh solutions of the same initial composition. The actual diffusion run was considered to begin at this time. After 4 to 6 days the solutions from the two compartments were analyzed for *n*-propanol content by a high-precision density determination technique (*16*). The integral diffusivities were then obtained by substitution in Equation 1. All measurements were made at a temperature of 25 ± 0.01° C.

RESULTS AND DISCUSSION

The integral diffusivities are given in Table I. The diffusivities which have theoretical and practical significance are, however, the differential values related to the integral values through the equation:

$$\bar{D} = \frac{1}{\bar{C}' - \bar{C}''} \int_{\bar{C}'}^{\bar{C}''} D dC \tag{2}$$

Equation 2 holds good for the present investigation where volume change on mixing is negligible (less than 0.09 ml. per gram mole mixture) (*16*). Rigorous equations, not requiring this assumption, have been derived by Dullien and Shemilt (*3*), and Olander (*13*). Using the graphical method of Stokes (*18*), and tabular integration, the differential diffusivities were obtained over the complete composition range and are presented in Table I.

The second column in Table I gives the value of the integral diffusivity as obtained by the simple logarithmic formula, Equation 1. The third column gives the mean *n*-propanol concentration (gram per ml.) over the run, while the fourth column contains the concentrations at which the integral diffusivities in the second column are equal to the true or differential diffusivities. The fifth column shows the mole fractions of *n*-propanol corresponding to the modified concentrations in column 4. These results are shown graphically in Figure 1 as integral dif-

Table I. Experimental Results

Cell/Run	$\bar{D} \times 10^5$	$C_{av.}$	C	x
V/7	2.024	0.025	0.025	0.043
VI/3	1.664	0.042	0.031	0.054
VI/5	1.409	0.049	0.041	0.071
V/4	1.134	0.124	0.087	0.146
V/6	1.028	0.154	0.124	0.205
V/3	0.990	0.184	0.135	0.223
IV/1	0.970	0.227	0.148	0.243
V/2	0.900	0.315	0.200	0.319
III/2	0.870	0.301	0.245	0.382
VI/2	0.857	0.393	0.410	0.597
III/1	0.895	0.406	0.500	0.701
V/5	0.980	0.555	0.585	0.792
V/8	1.100	0.648	0.647	0.855
VI/1	1.183	0.720	0.719	0.925
VI/4	1.289	0.779	0.778	0.980

fusivity against mean concentration, and in Figure 2 as differential diffusivity against mole fraction.

An error analysis showed the most probable error in the cell constant, estimated as $[(\delta\beta)/(\beta)] \times 100$, to be $\pm 0.3\%$. The observed error in cell constant determinations was less than $\pm 0.2\%$. For the *n*-propanol–toluene runs, the most probable error in concentration determination was estimated to be $\pm 0.0001_2$ gram per ml. The average probable error for all runs was estimated to be $\pm 0.5\%$ which compared very well with the observed error of $\pm 0.7\%$, indicating that the scatter of experimental values was due to the errors of analysis, and that significant sources of random error were absent or negligible.

Figures 1 and 2 show that there is almost four-fold variation of diffusivity over the entire composition range. The shapes of these curves are similar to those obtained in analogous systems such as methanol-benzene (*1*), methanol-toluene (*12*) and ethanol-benzene (*9*). The concentration-based diffusivity—i.e., the diffusivity as calculated using concentration as the diffusional driving force—shows a minimum of 0.84×10^{-5} cm.^{2} per second at about 0.5 mole fraction *n*-propanol, with values at infinite dilution of 3.56×10^{-5} and 1.35×10^{-5} cm.^{2} per second for pure toluene and pure *n*-propanol, respectively. The minimum diffusivity occurs in this system at a composition close to H. Lemonde's (*11*) reported minimum of 0.7×10^{-5} cm.^{2} per second at about 0.55 mole fraction ethanol in the ethanol-toluene system. Hydrogen bonding in alcohols and solute-solvent association are doubtless largely responsible for the wide variations in mutual diffusion rate with concentration in the binary systems mentioned above. These aspects of liquid nonideality are reflected in thermodynamic activity coefficients, and diffusivities should be calculated on the basis of chemical potential or activity as the driving force. For the case of a binary liquid system, the activity-based diffusion coefficient, D_a, is defined as follows (7):

$$D = D_a \frac{\partial \ln a}{\partial \ln x}$$

This type of correction for the diffusivity has been used in numerous semi-empirical relationships for evaluation of diffusivities from other physical data on the system. That of Hartley and Crank (*8*) is frequently employed when viscosity and thermodynamic data are available. In this system, however, no such data have been reported in the literature.

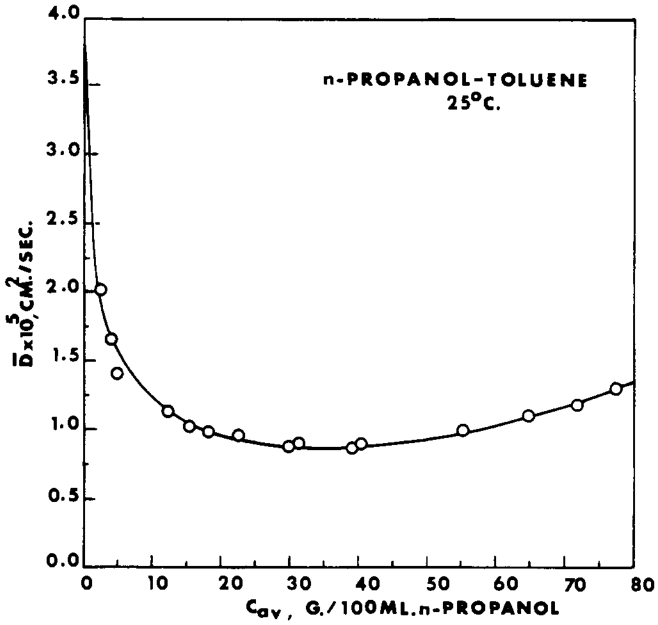

Figure 1. Variation of integral diffusivity with mean concentration of *n*-propanol for *n*-propanol–toluene system, at 25° C.

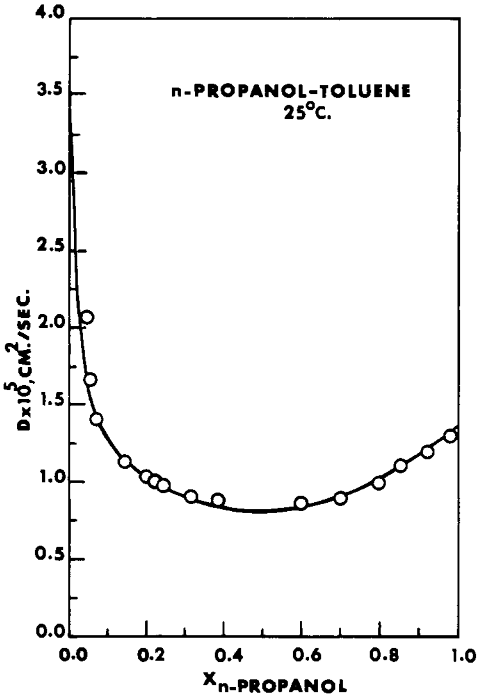

Figure 2. Variation of differential diffusivity with mole fraction *n*-propanol for *n*-propanol–toluene system, at 25° C.

The diffusivities at infinite dilution—i.e., the limiting values of D at the two ends of the composition range—were obtained both by smooth graphical extrapolation and by extension of the least-squares fit of experimental points to an analytical expression. For the toluene end (infinite dilution of *n*-propanol) the two methods agreed within 0.2×10^{-5} to give a limiting value of 3.56×10^{-5} cm.^{2} per sec., and for the propanol end, within 0.02×10^{-5} to give 1.35×10^{-5} cm.^{2} per second. Values were calculated foı this system by the correlations of Stokes-Einstein (*4*), Canjar (*10*), Othmer and Thakar (*14*), Scheibel (*15*), Wilke and Chang (*19*), and Sitaraman, Ibrahim, and Kuloor (*17*). Comparison of these with those derived experimentally are given in Table II, and indicated deviations ranging from 22 to 77%. This is not unexpected since the correlations are based on averages, often with wide deviations, and include major simplifying assumptions.

Additional work is planned which will provide the transport coefficients and the thermodynamic activity data which are now lacking on this and other nonideal systems.

Table II. Diffusivities at Infinite Dilution

Ref.	100 Mole % Toluene $D \times 10^5$ cm.^{2}/sec.	 Dev. from exptl., %	100 Mole % *n*-Propanol $D \times 10^5$ cm.^{2}/sec.	 Dev. from exptl., %
This work	3.56	0	1.35	0
(*4*)	1.08	70	0.35	67
(*10*)	1.44	60	1.64	22
(*14*)	1.96	45	0.53	61
(*15*)	2.15	40	0.32	77
(*19*)	2.70	24	0.52	62
(*17*)	2.32	35	0.57	58

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NOMENCLATURE

a = thermodynamic activity, mole fraction scale
$\bar{C}'$, $\bar{C}''$ = mean concentrations in the closed and open compartments, respectively, gram per ml.
ΔC_o, ΔC_f = initial and final concentration difference between the two compartments of the diffusion cell, gram per ml.
$\bar{D}$ = integral concentration-based diffusivity, cm.^{2} per sec.
D_a = activity-based differential diffusivity, cm.^{2} per sec.
D = concentration-based differential diffusivity, cm.^{2} per sec.
x = mole fraction *n*-propanol

Greek Letters

β = diaphragm cell constant, cm.$^{-2}$
θ = diffusion time, sec.

LITERATURE CITED

(1) Caldwell, C.S., Babb, A.L., *J. Phys. Chem.* **59**, 1113 (1955).
(2) Dullien, F.A.L., Shemilt, L.W., *Can. J. Chem. Eng.* **39**, 242 (1961).
(3) Dullien, F.A.L., Shemilt, L.W., *Trans. Faraday Soc.* **58**, 244 (1962).
(4) Einstein, A., *Ann. Physik* **17**, (4), 549 (1905).
(5) Fick, A., *Ann. Phys. Lpz.* **94**, 59 (1855).
(6) Gordon, A.R., *Ann. N. Y. Acad. Sci.* **46**, 285 (1945).
(7) Hartley, G.S., *Phil. Mag.* **12**, (7) 473 (1931).
(8) Hartley, G.S., Crank, J., *Trans. Faraday Soc.* **45**, 801 (1949).
(9) Johnson, P.A., Babb, A.L., *J. Phys. Chem.* **60**, 14 (1956).
(10) Kamal, M.R., Canjar, L.N., *A.I.Ch.E. J.* **8**, 329 (1962).
(11) Lemonde, H., *Ann. Phys.* **9**, 539 (1938).
(12) Nagarajan, R., M.Sc. thesis, University of New Brunswick, Fredericton, N. B., 1963.
(13) Olander, D.R., *J. Phys. Chem.* **67**, 1011 (1963).
(14) Othmer, D.F., Thakar, M.S., *Ind. Eng. Chem.* **45**, 589 (1953).
(15) Scheibel, E.G., *Ibid.*, **46**, 2007 (1954).
(16) Shroff, G.H., M.Sc. thesis, University of New Brunswick, Fredericton, N. B., 1965.
(17) Sitaraman, R., Ibrahim, S.H., Kuloor, N.R., J. CHEM. ENG. DATA **8**, 2 (1963).
(18) Stokes, R.H., *J. Am. Chem. Soc.* **73**, 3527 (1951).
(19) Wilke, C.R., Chang, P., *A.I.Ch.E. J.* **1**, 264 (1955).

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Solubilities of Disodium Terephthalate in Aqueous Solutions of Sodium Carbonate and Sodium Bicarbonate

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Solubility data have been obtained for disodium terephthalate in aqueous solutions of carbonate and sodium bicarbonate. The temperature range for carbonate was 40° to 91° C. and for bicarbonate, 40° to 66° C. At higher temperatures, the bicarbonate decomposed. The solubility changes due to temperature were insignificant. The data are shown in tabular form and by triangular phase diagrams.

THE SOLUBILTY of disodium terephthalate in aqueous solutions of sodium carbonate and sodium bicarbonate was determined. The temperature range covered for carbonate was 40° to 91° C. and for bicarbonate, 40° to 66° C. The sodium bicarbonate solutions were unstable at higher temperatures; the bicarbonate decomposed. With both systems, the solubility changes due to temperature were insignificant. The pH of the carbonate solutions was about 10.7 and that of the bicarbonate solutions, 8.1.

Smith and Hoebery (*4*) studied the solubility of disodium phthalate in solium carbonate solutions. Disodium phthalate is much more soluble than disodium terephthalate in water. This is true for the free acids also.

EXPERIMENTAL PROCEDURE

Apparatus. Samples were allowed to reach equilibrium in a shaking, constant-temperature bath. The bath used was a Model 2156-1 temperature-controlled water bath shaker, manufactured by Research Specialties Co., Richmond, Calif.

Reagents. SODIUM CARBONATE. Mallinckrodt Primary Standard grade.

SODIUM BICARBONATE. Mallinckrodt Analytical Reagent grade.

TEREPHTHALIC ACID. Eastman Kodak.

Preparation of Disodium Terephthalate. A 10% excess of the stoichiometric amount of sodium hydroxide to convert therephthalic acid to disodium terephthalate was mixed with terephthalic acid in distilled water. The quantity of water used was insufficient to dissolve all of the disodium terephthalate produced. The mixture was stirred for 24 hours, the disodium terephthalate was removed by filtering and was washed several times with a 1 to 2 mixture of water and methanol.

Sample Preparation and Sampling. The salt sloutions plus the solid phase salt were placed in rubber-stoppered Erlenmeyer flasks in the bath. Mineral oil was used as the bath

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