MEASUREMENT OF DIFFUSION IN BINARY NONELECTROLYTE SOLUTIONS BY THE DIAPHRAGM METHOD WITH *in situ* ANALYSIS. II.*

DIFFUSION IN TETRACHLOROMETHANE–BENZENE AND BENZENE–CYCLOHEXANE MIXTURES

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Certain theoretical conclusions of the Bearman statistical-mechanical theory of friction coefficients and some semiempirical formulas were verified on analytically expressed transport and thermodynamic properties of tetrachloromethane–benzene and benzene–cyclohexane mixtures. The disagreement between theory and experiments is relatively large, but smaller for the former than for the latter system as could be expected. Certain semiempirical formulas, however, perform well in estimating the dependences on concentration.

The theory of diffusion in liquid solutions of nonelectrolytes must explain not only the approved form of the Fick law but also predict the values of diffusion coefficients and to propose their dependence on the variables of state.

Results of many proposed theories of diffusion overlap with one another. Owing to the complexity of the problem, starting assumptions are often defined in an intuitive and unclear manner, so that it is often impossible to decide whether a theory involves another one or not[1,2].

The hydrodynamic theory of diffusion using friction coefficients[1-8] (based on the Maxwell-Stefan concept of diffusion) and its statistical-mechanical interpretation for regular solutions[1,8] give results in accord with other theories in the above-mentioned sense except for the exponential dependence of diffusion coefficients on temperature which follows from the theory of absolute reaction rates.

Such regular solutions (for exact definition see ref.[1,8]) are of course idealized; the theoretical results form nevertheless a basis of various semiempirical formulas and approximations.

The theoretical and semiempirical conclusions following from the theory of friction coefficients are verified in the present work on the tetrachloromethane–benzene and benzene–cyclohexane mixtures.

THEORETICAL

The phenomenological theory of friction coefficients in binary mixtures[1,2,8,11,12]

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yields the following expressions for the diffusion coefficient D and for the selfdiffusion coefficient D_i of i-th component (whose molar fraction is x_i):

$$D = QRTV/R_{12} , \qquad (1)$$

$$D_i = RTV/(x_iR_{ii} + x_jR_{12}) , \quad i,j = 1,2 \quad i \neq j , \qquad (2)$$

where R denotes gas constant, T absolute temperature, V molar volume of the mixture and Q thermodynamic factor defined as

$$Q \equiv 1 + \ln \gamma_1/\ln x_1 = 1 + \ln \gamma_2/\ln x_2 , \qquad (3)$$

where γ_i denotes activity coefficient.

In the limiting case of pure components one obtains $Q = 1$ by the Raoult law. The quantities R_{11}, R_{12} and R_{22} in Eqs (1) and (2) are friction coefficients, which are in general functions of temperature, pressure and concentration, and can be calculated from these equations.

Eqs (1) and (2) taken at the same temperature, pressure and composition can be combined to give

$$D = (D_1x_2 + D_2x_1) Q \left(\frac{x_2R_{12}}{x_1R_{11} + x_2R_{12}} + \frac{x_1R_{12}}{x_1R_{12} + x_2R_{22}} \right)^{-1} \qquad (4)$$

from where we obtain the physically understandable relation

$$\lim_{x_i \to 0} D = D_i^\infty \equiv \lim_{x_i \to 0} D_i \quad i = 1, 2 , \qquad (5)$$

where D_i^∞ means the selfdiffusion coefficient of component i at infinite dilution (On the other hand, the limiting value of D_i for $x_i \to 1$ is the coefficient of self-diffusion D_i^0 in pure i-th component.)

The statistical-mechanical treatment of the theory of friction coefficients after Bearman[1] leads to the conclusions for regular solutions that the ratio of the friction coefficients is independent of concentration and is equal to the ratio of molar volumes of pure components $(V_2^0/V_1^0)^{1.8}$:

$$R_{12}/R_{11} = R_{22}/R_{12} = V_2^0/V_1^0 , \qquad (6)$$

and further that the product of the selfdiffusion coefficient D_i and coefficient of (dynamic) viscosity η (both at the same temperature, pressure and composition) is independent of composition:

$$D_i\eta = D_i^0\eta_i = D_i^\infty\eta_j \qquad (7)$$

for $i, j = 1$ and 2, $i \neq j$; η_i and η_j are viscosities of pure components i and j. From Eq. (6) we obtain the relationship[2,14]

$$R_{12} = (R_{11}R_{22})^{1/2} , \qquad (8)$$

which reduces Eq. (4) to the Darken equation[15]

$$D = (D_1 x_2 + D_2 x_1) Q .$$ (9)

Introducing Eq. (7) into (9) we obtain the Carman–Stein equation[15,16]

$$D\eta = (D_1^\infty x_2 \eta_2 + D_2^\infty x_1 \eta_1) Q .$$ (10)

By introducing the constants σ_i (sometimes called friction coefficients[10,17])

$$\sigma_i \equiv RT/D_i^\infty N\eta_j, \quad i, j = 1, 2; \quad i \neq j ,$$ (11)

where N denotes Avogadro number, Eq. (10) can be rearranged to obtain the Hartley-Crank equation[15,18]:

$$D = (RT/N\eta)(x_2/\sigma_1 + x_1/\sigma_2) Q .$$ (12)

These relationships were obtained already earlier by simple hydrodynamic theories and by the theory of absolute reaction rates[15,19] according to which the σ_i value is related to the size of the diffusing molecule, hence it can be expected that the term $D\eta/QT$ depends only little on temperature. This is also expressed by the Einstein–Stokes law, *cf.* Eq. (11). A similar conclusion follows from statistical mechanics under considerable
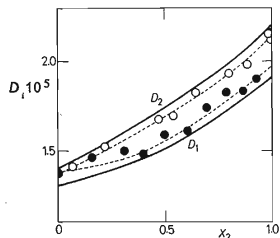

FIG. 1

Selfdiffusion Coefficients D_i (cm²/s) ($i = 1, 2$) in Tetrachloromethane(1)–Benzene(2) Mixtures at 25°C

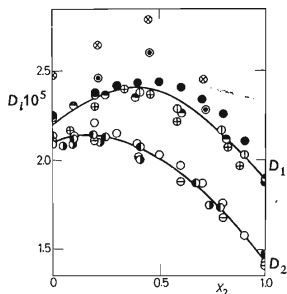● Tetrachloromethane ref.[35]; ○ benzene ref.[34]; full lines express the used dependences.

FIG. 2

Selfdiffusion Coefficients D_i (cm²/s) ($i = 1, 2$) in Benzene(1)–Cyclohexane(2) Mixtures at 25°C

◑ ○ ⊖ ◐ Cyclohexane; ⊕ ● ① ⊜ ⊙ benzene; ⊗ benzene at 35°C; ◑ ⊕ ref.[8]., ⊝ ⊘ ref.[11], ○ ● ref.[12], ⊙ ⊗ ref.[29], ◐ ⊖ ref.[33]; full lines express the dependences.

simplifications[13]. The mentioned equations serve as a base for semiempirical estimation of the dependence of the D value on concentration as well as of the D value in dilute solutions.

Approximation of Eq. (12) involve in general σ_i coefficients dependent on composition. Its zero-order approximation involves σ_i values independent of composition and calculated from Eq. (11); it is therefore equivalent to Eq. (10).

The first approximation of Eq. (12) involves the assumption[17] that σ_i changes linearly between two extremes, σ_i^∞ and σ_i^0, defined by the relations

$$RT/N\sigma_i^\infty = \eta_j D_i^\infty , \quad RT/N\sigma_i^0 = \eta_i D_i^0 , \qquad (13), (14)$$

for $i, j = 1$ or 2, $i \neq j$. The second approximation of Eq. (12) involves the assumption[10] that the relation

$$\Delta\sigma_i/\sigma_i^{(1)} = k_i \delta\eta/\eta^{(1)} , \quad i = 1, 2 , \qquad (15)$$

verified experimentally for dilute solutions[10], holds in the whole concentration range. Here $\sigma_i^{(1)}$ stands for the value obtained as a first approximation, $\delta\eta = \eta - \eta^{(1)}$, $\eta^{(1)} \equiv \eta_1 x_1 + \eta_2 x_2$, $\Delta\sigma_i = \sigma_i - \sigma_i^{(1)}$ and σ_i is the second approximation which is to be found. The constant k_i is determined from measurements at low concentrations where the ratio x_i/x_j is small, hence σ_j can be set equal to the value from the first approximation.

The Harned approximation[20] of Eq. (12) is based on the so-called Sandquist

TABLE I

Limiting Diffusion Coefficients $D . 10^5$ (cm^2/s)

°C	$x_2 = 0$	$x_2 = 1$
Tetrachloromethane(1)–benzene(2)		
25	1·402	1·905
40	1·783	2·458
Benzene(1)–cyclohexane(2)		
25	2·1044	1·8825
35	2·477	2·207
40	2·618[a]	—

[a] Estimated by extrapolation from Table I in ref.[28].

TABLE II

Selfdiffusion Coefficients $D_i^0 . 10^5$ (cm^2/s) in Pure Substances

Substance	Temperature, °C		
	25	35	40
C_6H_6[a]	2·20	2·50	2·69
C_6H_{12}[b]	1·42	1·74	—
CCl_4[c]	1·31	—	1·82

[a] At 25°C from 6 data[8] and[11,12,29,30], otherwise from 3 data[31] and[30]. [b] At 25°C from 5 data[8] and[11,12], at 35°C from ref.[32] [c] At25°C from 3 data[31] and[17], at 40°C from 2 data[31].

extrapolation[17,21], according to which we have for dilute solutions

$$D\eta/Q = D_i^\infty \eta_j + l_i(\eta - \eta_j),$$ (16)

for $i, j = 1$ or 2, $i \neq j$; l_i is a constant. According to Eq. (12) we have for dilute solutions $D\eta/Q = RT/N\sigma_1$, which on introducing into (16) and extrapolating to the whole concentration range gives the Harned approximation[20]

$$1/\sigma_i = 1/\sigma_i^\infty + (N/RT) l_i(\eta - \eta_j),$$ (17)

for $i, j = 1$ or 2, $i \neq j$; σ_i^∞ is defined by Eq. (13) and l_i is determined for a dilute solution.

McCall and Anderson[11] proposed an empirical approximation of the Darken equation (9):

$$D = (D_1 x_2 + D_2 x_1) \eta/(x_1\eta_1 + x_2\eta_2).$$ (18)

For dilute solutions, we shall verify some semiempirical formulas based on the Einstein-Stokes equation. The following relationship was proposed by Othmer and Thakar[22]:

$$D = 14.0 \cdot 10^{-5}/(V_i^0)^{0.6} \eta_j \eta_w^{1.1 L_j/L_w}, \quad (cm^2 s^{-1})$$ (19)

where η_w denotes viscosity of water at a given temperature (in cP), η_j viscosity of solvent at 20°C (cP), L_j heat of evaporation of solvent (cal/mol), L_w heat of evaporation of water (cal/mol), and V_i^0 molar volume of the dissolved substance (ml/mol). Wilke and Chang[23] proposed the equation

$$D = 7.4 \cdot 10^{-8} T(M_j\psi)^{1/2}/(V_i^0)^{0.6} \eta_j, \quad (cm^2 s^{-1})$$ (20)

where ψ denotes association parameter, equal to unity for nonpolar substances, V_i^0 molar volume of dissolved substance at normal boiling point (cm³/mol), M_j molar mass of solvent, T absolute temperature (°K) and η_j viscosity of solution (cP), practically equal to viscosity of solvent. Eq. (20) was modified by Reddy and Doraiswamy[24]:

$$D = \bar{K} M_j^{1/2} T/\eta_j (V_i^0 V_j^0)^{1/3}; \quad (cm^2 s^{-1})$$ (21)

here $\bar{K} = 10 \cdot 10^{-8}$ or $8.5 \cdot 10^{-8}$ for $V_j^0/V_i^0 \leqq 1.5$ or > 1.5, respectively, V_j^0 denotes molar volume of solvent (cm³/mol), V_i^0 denotes molar volume of solute (cm³/mol), η_j viscosity of solvent (cP) and other symbols have the same meaning as in Eq. (20). The theory of absolute reaction rates[19] gives, besides results similar to the preceding ones, an exponential dependence of the diffusion coefficient on temperature:

$$D = D_0 \exp(-E_D/RT),$$ (22)

where D_0 denotes frequency factor for diffusion and E_D activation energy of diffusion. The latter should be $\frac{1}{4}$ to $\frac{1}{3}$ as large as the heat of evaporation and by about the RT

value larger than the activation energy of viscosity, E_η, obtained from an analogous exponential dependence[15,19]:

$$\eta = \eta_0 \exp\left(E_\eta/RT\right), \tag{23}$$

where η_0 is the frequency factor for viscosity.

Vignes[25] proposed an equation according to which the term $\log\left(D/Q\right)$ is a linear

FIG. 3

Comparison of Experimental and Theoretical Dependences of Diffusion Coefficients D (cm^2/s) on Concentration

Full lines are experimental dependences (24)—(27); ... zeroth (10), — — — first (13), (14), — . — . — . — second (15) approximation of Eq. (12).
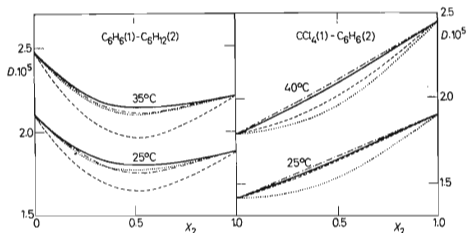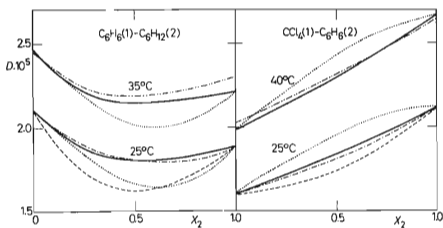
FIG. 4

Comparison of Experimental and Theoretical Dependences of Diffusion Coefficients D (cm^2/s) on Concentration

Full lines are experimental dependences (24)—(27); ... Eq. (17), — — — Eq. (9), — . — . — . . — Eq. (18), — . . — . . — . . — Einstein–Stokes equation.

function of the molar fraction. This can be derived from the theory of absolute reaction rates on the assumption of additivity of activation energies[26].
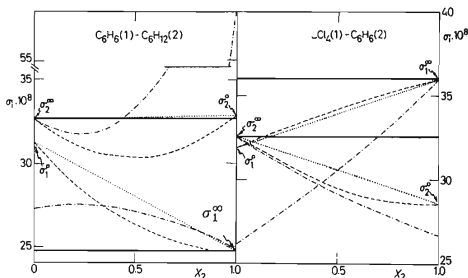

Fig. 5

Dependence of Coefficients of Equation (12) σ_i (cm) on Concentration at 25°C

Full lines correspond to equation (10); ... first (13) (14), — — — second (15), — . — . — . — Harned approximation (17).

PROPERTIES OF SYSTEMS UNDER DISCUSSION AND THEIR CORRELATIONS

Diffusion

The data of Caldwell and Babb[9] were used for the *tetrachloromethane(1)–benzene(2) system* at 25 and 40°C. Since these data do not refer exactly to 25°C, they were corrected by means of Eq. (22); the activation energy was determined from the cited work[9] (*cf.* Table VII). The correlation after Vignes[25] assuming $Q = 1$ gives

$$\log (10^5 D) = 0.14687 + 0.13304 x_2 \quad (25°C) , \tag{24}$$

$$\log (10^5 D) = 0.25120 + 0.13945 x_2 \quad (40°C) . \tag{25}$$

The mean deviation does not exceed 1%, a value given in ref.[9].

For the benzene(1)–cyclohexane(2) system we made an empirical correlation with a polynomial of third degree[27]. The data at 25°C were taken from ref.[10] (see also Harned[20]):

$$10^5 D = 2.10441 - 1.32323 x_2 + 1.73416 x_2^2 - 0.63289 x_2^3 \quad (25°C) . \tag{26}$$

The mean deviation is about $\frac{1}{3}$ of the error of measurement, 0.2%, given in ref.[10] The data at 35°C were taken from the preceding work (Table I in ref.[28]), however, the correlation with the polynomial was reasonable only up to 85% cyclohexane; for higher concentrations a linear dependence was used, namely a tangent to the polynomial in the point corresponding to 85% cyclohexane:

$$10^5 D = 2.4767 - 1.5562 x_2 + 2.2617 x_2^2 - 0.9841 x_2^3, \quad 0 \leqq x_2 \leqq 0.85 ,$$
$$10^5 D = 2.1836 + 0.1556(x_2 - 0.85) , \quad 0.85 \leqq x_2 \leqq 1 \quad (35°C) . \tag{27}$$

The mean deviation of the measured data from those calculated from Eq. (27) is about 1%. Limiting diffusion coefficients (for $x_2 = 0$ and $x_2 = 1$) calculated from Eqs (24)−(27) are given in Table I.

Coefficients of Selfdiffusion

The coefficients of selfdiffusion, D_i^0, in pure substances were obtained as arithmetic mean of the data of various authors (Table II). The selfdiffusion coefficients at 25°C found in the literature for the benzene–cyclohexane[8,11,12,29,33] (except for selfdiffusion of benzene at 35°C[29]) and tetrachloromethane–benzene[34,35] systems are shown graphically in Figs 1 and 2. Since no analytical expression is available for correlation, the selfdiffusion coefficients necessary in the calculations were determined from a smoothed curve drawn through the experimental points so that the extreme points were in accord with the more reliable data from Tables I and II. With the tetrachloromethane–benzene system, the curves were therefore shifted (Fig. 1). The mean deviation of the coefficients of selfdiffusion is estimated as 5%.

Viscosity

Consistent data for the studied systems at 25°C are available[10,36,37]. Linke[38] measured the viscosity at various temperatures but his data interpolated to 25°C are systematically lower; therefore they were used only in calculating the activation energies from Eq. (23). The latter values were then used in correcting the data at 25°C[10,36,37] for a higher temperature. The calculation according to ref.[39] gives the following expressions for the dynamic viscosity η (cP):

Tetrachloromethane(1)–benzene(2), 25°C
$$\log (10^3 \eta) = 2{\cdot}95516(1 - x_2) + 2{\cdot}77786x_2 + 0{\cdot}01515x_2(1 - x_2) \qquad (28)$$

Tetrachloromethane(1)–benzene(2), 40°C
$$\log (10^3 \eta) = 2{\cdot}86283(1 - x_2) + 2{\cdot}69000x_2 + 0{\cdot}01622x_2(1 - x_2) \qquad (29)$$

Benzene(1)–cyclohexane(2), 25°C
$$\log (10^3 \eta) = 2{\cdot}94724x_2 + 2{\cdot}77786(1 - x_2) - 0{\cdot}30491x_2(1 - x_2) \qquad (30)$$

Benzene(1)–cyclohexane(2), 35°C
$$\log (10^3 \eta) = 2{\cdot}87553x_2 + 2{\cdot}72329(1 - x_2) - 0{\cdot}27891x_2(1 - x_2) \,. \qquad (31)$$

The mean deviation in η values at 25°C is about 0·1%, at higher temperatures about 1% (cf.[10,29,36−38]).

Density

The following functions[42] fit the density data, $\varrho(g/cm^3)$, for the tetrachloromethane–benzene[40,53] and benzene–cyclohexane[10,41] systems:

Tetrachloromethane(1)–benzene(2), 25°C
$$\varrho = 1{\cdot}5844(1 - x_2) + 0{\cdot}8737x_2 + 0{\cdot}058364x_2(1 - x_2) \qquad (32)$$

Tetrachloromethane(1)–benzene(2), 40°C
$$\varrho = 1{\cdot}5550(1 - x_2) + 0{\cdot}8576x_2 + 0{\cdot}056235x_2(1 - x_2) \qquad (33)$$

Benzene(1)–cyclohexane(2), 25°C

$$\varrho = 0{\cdot}87367(1 - x_2) + 0{\cdot}77358x_2 + x_2(1 - x_2)(-4{\cdot}51707 \times 10^{-2} + 5{\cdot}23730 \,.\, 10^{-3}x_2)$$

$$(34)$$

Benzene(1)–cyclohexane(2), 35°C

$$\varrho = 0{\cdot}86309(1 - x_2) + 0{\cdot}76431x_2 + x_2(1 - x_2)(-4{\cdot}48360 \times 10^{-2} + 8{\cdot}70288 \,.\, 10^{-3}x_2)$$

$$(35)$$

Benzene(1)–cyclohexane(2), 40°C

$$\varrho = 0{\cdot}85771(1 - x_2) + 0{\cdot}75952x_2 + x_2(1 - x_2)(-4{\cdot}44382 \times 10^{-2} + 8{\cdot}51168 \,.\, 10^{-3}x_2)$$

$$(36)$$

The deviation does not exceed 0·05%.

Thermodynamic Q Factor

The Q factor, defined by Eq. (3), was calculated by deriving the Margules two-constant equation[43] whose constants were obtained by interpolation of the linear dependence of the logarithm of limiting relative volatility on the logarithm of component vapor pressure[44,45]. This method is based on measurement in the studied systems at various temperatures[45−48]. The results are:

Tetrachloromethane(1)–benzene(2), 25°C

$$Q = 1 - x_2(1 - x_2)(0{\cdot}29239 - 0{\cdot}10612x_2) \,. \qquad (37)$$

Tetrachloromethane(1)–benzene(2), 40°C

$$Q = 1 - x_2(1 - x_2)(0{\cdot}26360 - 0{\cdot}06591x_2) \,. \qquad (38)$$

Benzene(1)–cyclohexane(2), 25°C

$$Q = 1 - x_2(1 - x_2)(1{\cdot}21157 - 0{\cdot}31091x_2) \,. \qquad (39)$$

Benzene(1)–cyclohexane(2), 35°C

$$Q = 1 - x_2(1 - x_2)(1{\cdot}11433 - 0{\cdot}30068x_2) \,. \qquad (40)$$

The deviation in Q values is about 4% (based on Q values in ref.[10] and on measurement of activity coefficients at 25°C in the CCl_4–C_6H_6 system[49]).

The remaining data, necessary to check the relationship in the theoretical part, are summarized in Table III. The heats of evaporation were taken from ref.[50], densities at normal boiling point are interpolated data of ref.[51] and the properties of water in Eq. (19) are tabulated values[52].

RESULTS AND DISCUSSION

The mentioned analytical expressions were used in verification of the theoretical relationships. The results are shown graphically in Figs 3−5 and in Tables IV−VII. With respect to accuracy of the properties under study, we can consider the agreement between experimental and calculated diffusion coefficients as good when the mean deviation is about 4%; if selfdiffusion coefficients are involved then about 8% (estimation based on Eqs (9) and (12)). In judging the conclusions of the Bearman theory[1], Eqs (6)−(12), it is necessary to take into account that the systems do not obey exactly the definition of regular solutions[1,8]. However, it can be expected that

the agreement will be better for the tetrachloromethane–benzene system, which is close to a regular solution, than for benzene–cyclohexane[47,48], as is actually the case (*cf.* Figs 3 and 4 and Tables IV and V). The same tendency may be found with approximations (14), (15), (17) and (18). For both systems the second approximation (15) and the McCall–Anderson equation (18) perform best. For carbon tetrachloride–benzene the first approximation (13), (14) and the Darken equation (9) hold good, whereas the Carman–Stein equation (10) and Harned approximation (17) are only still acceptable similarly as the Darken equation (9) for benzene–cyclohexane, where on the contrary Eqs (13), (14) and (17) do not hold. For this system, the Carman-Stein equation (10) (zeroth approximation) holds surprisingly good.

The mentioned approximations were verified mainly on the benzene–cyclohexane system at 25°C by other authors[5,8,10,11,33] with whom our results are in good

TABLE III
Some Properties of Components

Value	C_6H_6	CCl_4	C_6H_{12}
Molar mass	78·115	153·823	84·163
Heat of evaporation at n.b.p., cal/mol	7 353	7 161	7 190
Molar volume at n.b.p. cm³/mol	95·92	103·72	116·91

TABLE IV
Verification of Equations (7)[a]

Term	$CCl_4(1)$–$C_6H_6(2)$		$C_6H_6(1)$–$C_6H_{12}(2)$	
	25°C	40°C	25°C	35°C
$\eta_1 D_2^\infty . 10^7$	1·264	1·300	1·262	1·310
$\eta_2 D_2^0 . 10^7$	1·319	1·376	1·258	1·306
$\eta D_2 . 10^7 (x_2 = 0,5)$	1·291	—	1·223	—
$\eta_2 D_1^\infty . 10^7$	1·142	1·257	1·667	1·657
$\eta_1 D_1^0 . 10^7$	1·181	1·327	1·319	1·322
$\eta D_1 . 10^7 (x_2 = 0·5)$	1·128	—	1·461	—

[a] Data in the cm–g–s system.

TABLE V

Verification of Equations (6), (8)^a

x_2	Equation (8)				Equation (6)		
	$R_{11} \cdot 10^{17}$	$R_{22} \cdot 10^{17}$	$R_{12} \cdot 10^{17}$	$\sqrt{(R_{11}R_{22})} \cdot 10^{17}$	R_{12}/R_{11}	R_{22}/R_{12}	V_2^0/V_1^0
			$CCl_4(1)$-$C_6H_6(2)$				
0	1·837	—	1·717	—			
0·2	1·765	1·665	1·519	1·714	0·861	1·096	
0·4	1·725	1·428	1·376	1·569	0·798	1·038	
0·6	1·698	1·243	1·286	1·453	0·757	0·967	0·921
0·8	1·615	1·113	1·216	1·337	0·753	0·915	
1	—	1·007	1·164	—			
			$C_6H_6(1)$-$C_6H_{12}(2)$				
0	1·008	—	1·054	—			
0·2	0·993	1·445	0·996	1·198	1·003	1·451	
0·4	1·017	1·445	0·989	1·212	0·972	1·461	
0·6	1·133	1·495	1·057	1·301	0·933	1·414	1·217
0·8	1·310	1·609	1·206	1·452	0·921	1·334	
1	—	1·899	1·433	—			

^{a} Data in the cm–g–s system; 25°C.

TABLE VI

Estimation of Limiting Diffusion Coefficients, $D \cdot 10^5$ (cm^2/s) from Semiempirical Equations (19)—(21)

Solute	Solvent	°C	Exp. data^a	Eq. (19)	Eq. (20)	Eq. (21)
C_6H_6	CCl_4	25	1·402	1·06	1·96	2·00
CCl_4	C_6H_6	25	1·905	1·54	2·01	2·14
C_6H_6	CCl_4	40	1·783	1·35	2·55	2·56
CCl_4	C_6H_6	40	2·458	1·97	2·58	2·72
C_6H_{12}	C_6H_6	25	2·104	1·43	1·87	2·06
C_6H_6	C_6H_{12}	25	1·883	1·07	1·48	1·45
C_6H_{12}	C_6H_6	35	2·477	1·70	2·20	2·40
C_6H_6	C_6H_{12}	35	2·207	1·26	1·80	1·75
C_6H_{12}	C_6H_6	40	2·618	1·83	2·40	2·62

^{a} See Table I.

TABLE VII

Activation Energy of Diffusion, E_D and Viscosity E_η (kcal/mol) and Heat of Evaporation ΔH (kcal/mol)

x_2	E_D	E_η	ΔH	x_2	E_D	E_η	ΔH
	$CCl_4(1)–C_6H_6(2)$				$C_6H_6(1)–C_6H_{12}(2)$		
0	2·97	2·63	7·16	0	2·84	2·29	7·35
0·5	3·06	2·52	—	0·5	3·20	2·35	—
1	3·16	2·50	7·35	1	2·90	3·01	7·19

agreement except for the Harned approximation[20] (17) (Fig. 4; cf. the dependence of σ_i coefficients on composition in Fig. 5 for the Harned approximation).

It is seen from Tables IV and V that the rule (8) does not hold for the mentioned systems (according to the estimation of errors the deviations should be within $\pm 4\%$) similarly as (6) and (7). Again the deviations are greater for the benzene–cyclohexane system than for tetrachloromethane–benzene.

The assumption that the term $D\eta/QT$ is independent of temperature (denoted as Einstein-Stokes law in Fig. 4) is in accord with measurements within the limits of experimental errors. This, together with a similar course of the approximate relationships at different temperatures, is in favour of the newly measured data for benzene–cyclohexane at 35°C [7,28].

The semiempirical relationships for limiting diffusion coefficients $(19)–(21)$ are not accurate enough, as seen from Table VI. The activation energies of diffusion and viscosity calculated from Eqs (22) and (23) are compared with the heat of evaporation in Table VII and are in rough agreement with the theory of absolute reaction rates[9] (cf. discussion of Eq. (22)).

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