Temperature and Concentration Dependence of Mutual Diffusion Coefficients of Some Binary Liquid Systems

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Mutual diffusion coefficients are measured for ethanol–water, acetone–water, and acetone–chloroform systems by means of a three-compartment cell. In each case, the results cover the complete concentration range and temperatures from 25°C to around the normal boiling point. The diffusion coefficients at the terminal concentrations and those at the normal boiling point are obtained by extrapolation of the experimental values. The uncertainty of the experimental diffusion coefficients is estimated to be ±2.6%. These results are compared with the results computed from various prediction correlations.

Most mass transfer and heat transfer calculations in chemical engineering employ mutual diffusion coefficients at the ambient and at the higher temperatures. These data are scarce because of experimental difficulties of measurement, particularly at the higher temperatures.

In this report mutual diffusion coefficients measured for three binary systems: ethanol–water, acetone–water, and acetone–chloroform over the whole range of concentrations and temperatures ranging from 25°C to approximately the respective boiling points are presented. The measurements were made with the three-compartment cell developed by these authors (*3*). Four sets of data for the ethanol–water system (*6, 9, 19, 25*) at 25°C and two sets of data (*19, 25*) at higher temperatures were found in the literature. These were used for comparison with the data obtained in this work.

From the existing prediction correlations, those of Leffler and Cullinan (*14*) and of Vignes (*32*) were selected to compare their predicted coefficients with the experimental coefficients. The prediction methods for the diffusion coefficients at infinite dilution of Wilke and Chang (*34*), King et al. (*13*), and of Sitaraman et al. (*24*) were also checked against the diffusion coefficients obtained by extrapolation of the experimental diffusion coefficients.

Diffusion Cell

A three-compartment cell developed by these authors is described in ref. *3*. In the same reference, detailed operating instructions are given, and possible experimental errors are indicated. In this report only the chief features of the cell are discussed with the aid of Figure 1.

The cell constitutes a modification of the well-known diaphragm cell used by Stokes (*26*) and other workers and described in refs. *10* and *26*. The aim of modifications was to adapt it for operation at temperatures higher than the ambient temperature. Some attempts to construct such a cell were made (*4, 23*).

The three-compartment cell is operated under a slight pressure in order to avoid boiling as this would interfere with the process of diffusion through the sintered glass diaphragm. If any evaporated solvent passes up the connecting tubes Ii, Kk, Jj, it is condensed and returned to the tubes H, G and compartment A. In order to effect the condensation, the tubes above the points J, K, I are kept in a stream of cooling air. In practice no condensate was noticed in these tubes even at the highest operating temperature of 85°C. A constant operating temperature is maintained by keeping the cell immersed in a thermostat bath. The pressures used in the cell were always below 20 psig which is too low to have any significant effect on the diffusion coefficient. The necessary pressure is exerted by connecting the cell through the tubes Jj, Kk, Ii to a cylinder containing an inert gas such as nitrogen.

Another feature of the cell is that during the preheating period, the test liquids are kept in compartments A and C so that there is no chance of any diffusion taking place, compartment B being filled with mercury during that time.

Accuracy of Experimental Results

The errors in the diffusion coefficient owing to the design and operating method of the cell were considered in great detail (*5*), and a figure of 0.1% was estimated for experiments with the system ethanol–water.

All the errors of measurement such as in the analysis of solutions, in the volumes of test liquids charged, and in the setting of the levels in the cell, ultimately contribute to the error in the concentrations of the test liquids. The error in the diffusion coefficient owing to these caus-

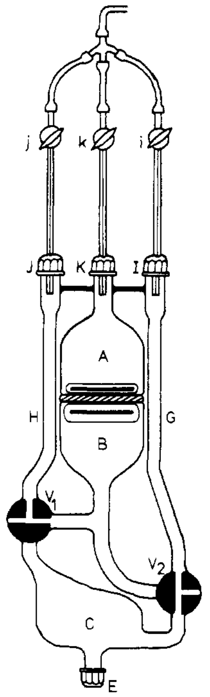

Figure 1. General arrangement of three-compartment diffusion cell

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es was calculated by the method recommended by Levitt (*15*). It is a function of the magnitude of the diffusion coefficient and of the difference in the concentrations in the two compartments of the cell (compartment A and B of Figure 1) (*3*). Thus, it varies from approximately 1% for the largest difference to approximately 2% for the lowest difference used in this investigation. It is suggested that an allowance of 0.5% is made for the unaccountable factors giving an overall maximum error of 2.6%. This figure will be adopted as the experimental error of the diffusion coefficients for the systems ethanol–water and acetone–water for which a density method of concentration determination was used. A refractive index method of analysis was adopted for the system acetone–chloroform, but the overall error in the diffusion coefficient amounts to the same figure of 2.6%.

This degree of accuracy is consistent (*30*) with the deviation of the ethanol–water data from the average values obtained for four sets of data at 25°C so far available: Hammond and Stokes (*9*), Dullien and Shemilt (*6*), Pratt and Wakeham (*19*), and the present data (*30*). The data of Smith and Storrow (*25*) were not used in the calculation of the average values as their results differ considerably from those of the remaining authors.

Solvents and Their Physical Properties

Analytical reagent grade ethanol, acetone, and chloroform and double distilled water were used to prepare the test solutions. $AgNO_3$ and KCl solutions required for periodic calibrations of the diffusion cell were also of analytical reagent grade. Before being charged into the cell, the test solutions were refluxed to remove any residual air present.

The required physical properties of the solvents and of their various mixtures were obtained from the literature whenever possible. Extrapolations and interpolations were often used to obtain these properties at the required temperature and concentration. When these properties were not available in the literature, they were determined experimentally in this laboratory (*30*). (Tables of physical properties and primary experimental data from ref. *30* are included in the Appendix which has been deposited with the ACS Microfilm Depository Service.) Table I indicates the properties used in the calculation of experimental results and the properties used in checking various prediction correlations. A literature reference to these physical properties is also indicated in Table I.

Experimental Results

The experimental observations were used to calculate integral diffusion coefficients by means of the relationship recommended by Holmes (*10*):

$$\bar{D}_{AB} = \frac{1}{\beta t}\log\left(\frac{C_1 - C_2}{C_3 - C_4}\right) \qquad (1)$$

These coefficients were converted into differential coefficients using the method of Dullien and Shemilt (*6*).

Such differential coefficients for the three binary systems are presented in Tables II and III. The diffusion coefficients at the terminal concentrations, shown in these tables, were obtained by graphical extrapolation of the experimental values. The diffusion coefficients for the concentrations: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 were obtained by graphical interpolation. The interpolation distances were very short in each case; therefore, the accuracy of the values obtained is about the same as that for the coefficients derived from measurements.

There are four sets of experimental diffusion coefficients in existence for the system ethanol–water at 25°C. These and our own data are shown in Table II. The agreement between our own data and those of Dullien and Shemilt (*6*), Hammond and Stokes (*9*), and Pratt and Wakeham (*19*) is good, the average deviation from our data being 0.3%, 1.3%, and 5.0%, respectively. On the other hand, the data of Smith and Storrow (*25*) differ considerably with an average deviation of ±50%.

Two sets of experimental data for the system ethanol–water at higher temperatures were found in the literature (*19, 25*). The comparison with our own data is made difficult because of different temperatures and different

Table I. Sources of Required Physical Properties

	Viscosity	α_A[a]	$\rho_{AB} - x_A - T$ relationship[b]	[*P*]	ΔH	*V*
Ethanol	*29*	...	...	*20*	*21*	*21*
Water	*29*	...	...	*5*	*21*	*21*
Ethanol–water	*29*[c]	*7, 8, 12, 33*	*18, 29*	...	...	...
Acetone	*11*	...	...	*20*	*21*	*21*
Acetone–water	*11*[c]	*27*	[d], *28*	...	...	...
Chloroform	*1, 17*	...	...	*20*	*21*	*21*
Acetone–chloroform	*1, 17*	*16, 22*	[d], *29*	...	...	...

[a] Available in the reference or calculated from the vapor-liquid equilibrium data provided in the reference. [b] $D_{AB}°$, and $D_{BA}°$ values for all three systems are in Table III. [c] Extrapolation or interpolation involved. [d] Determined experimentally in this laboratory (*30*).

Table II. Differential Diffusion Coefficients of Various Authors for Ethanol–Water System at 25°C

Mole fraction x_A	Differential diffusion coefficient, $D_{AB} \times 10^5$, cm²/sec				
	T – W[a]	D – S[b]	H – S[c]	P – W[d]	S – S[e]
0.000[f]	1.250	1.220	1.240	1.240	1.313
0.014	...	1.096	...	...	...
0.020	...	...	1.080	...	...
0.026	1.076	...	...	...	...
0.050	...	...	...	0.900	...
0.152	...	...	...	0.460	...
0.229	...	...	...	0.390	...
0.266	0.368	...	...	...	...
0.276	...	0.377	0.362	...	...
0.279	...	...	...	...	0.403
0.308	...	...	...	0.335	...
0.390	...	...	...	...	0.520
0.394	...	0.423	0.407	...	...
0.408	0.405	...	...	...	...
0.439	...	...	...	0.500	...
0.635	...	...	...	0.755	...
0.680	0.745	0.747	0.766	...	...
0.680	0.743	...	...	...	...
0.680	0.743	...	...	...	...
0.742	...	...	...	...	1.480
0.812	...	...	...	0.930	...
0.842	...	1.010	...	...	...
0.844	...	...	0.981	...	...
0.880	1.047	...	...	...	...
0.944	1.131	...	...	...	...
0.948	...	...	...	...	2.150
1.000[f]	1.220	1.220	1.132	1.080	2.360

[a] This work. [b] Dullien and Shemilt (*6*). [c] Hammond and Stokes (*9*). [d] Pratt and Wakeham (*19*). [e] Smith and Storrow (*25*). [f] Diffusion coefficients at $x_A = 0$ and $x_A = 1$ were obtained by extrapolation.

concentrations being used in almost all cases. To effect the comparison the method adopted was that of plotting our own data and then superimposing the literature data after they had been readjusted first to the same temperature base. The following relationship (1):

$$\frac{\ln D_{AB}}{(1/T)} = \text{constant for a given concentration} \qquad (2)$$

was employed to make the temperature corrections. In each case, the temperature correction involved only a few degrees; therefore, the approximate nature of Equation 2 could not introduce any significant error. Inspection of Figure 2 shows that the data of Pratt and Wakeham (19) agree very closely with our own for the lower concentrations and at all the temperatures. At the higher concentrations and particularly at higher temperatures, their data give generally higher coefficients, and the curves tend to exhibit a convexity in the ethanol-rich end. The maximum deviation for each isotherm increases with temperature, being +12% at 25°C and +36% at 73°C, and it occurs at a concentration of approximately 0.6 mole fraction. No explanation for these deviations can be offered at present. The data of Smith and Storrow (25) do not show any consistency, and their magnitude differs considerably from the data of the remaining authors.

There is only one set of data for the system acetone-water at 25°C, that of Anderson et al. (1). This is compared with our data in Figure 3, and it is obvious that the agreement is satisfactory, the largest deviation from our data being 2%. There are no literature data available for this system at higher temperatures.

Also, Anderson et al. (1) provided experimental diffusion coefficients for the system acetone-chloroform at 25° and 40°C. A comparison is made in Figure 4, and again the agreement is satisfactory, the largest deviation being 3%. The comparison with the Anderson et al. (1) data is particularly encouraging as their diffusion coefficients were obtained by the Mach Zender diffusiometer (2) which is a completely different measuring technique from that used in this investigation.

Equation 2 was also used to obtain diffusion coefficients at the normal boiling points for each system. These results are tabulated in Table IV.

Discussion and Test of Some Prediction Equations

A number of prediction correlations for mutual diffusion coefficients are available in the literature (30). Those of Leffler and Cullinan (14) and of Vignes (32) have some theoretical basis and have been tested by many authors, but unfortunately, only with experimental data for the ambient temperatures. These correlations have, however, some limitations. Leffler and Cullinan (14) recommended their equation for ideal systems and for nonideal and nonassociating systems. It is not suitable for the associat-

Table III. Differential Diffusion Coefficients for Systems Ethanol-Water, Acetone-Water, and Acetone-Chloroform

Mole fraction ethanol x_A	$D_{AB} \times 10^5$, cm²/sec 40°C	58°C	73°C	85°C
	Ethanol-water			
0.000[a]	1.700	2.400	2.950	3.503
0.024	1.510	2.143	2.550	3.270
0.100[a]	1.000	1.500	1.900	2.470
0.144	0.780	1.220	1.610	2.110
0.200[a]	0.680	1.020	1.420	1.835
0.254	0.635	0.931	1.360	1.725
0.300[a]	0.610	0.930	1.340	1.740
0.400[a]	0.640	1.020	1.420	1.980
0.500[a]	0.730	1.185	1.610	2.285
0.590	0.850	1.360	1.830	2.560
0.600[a]	0.865	1.380	1.860	2.600
0.680	1.020	1.550	2.100	2.860
0.700[a]	1.060	1.590	2.170	2.930
0.792	1.260	1.792	2.430	...
0.800[a]	1.275	1.810	2.490	...
0.880	1.440	2.010	2.750	...
0.900[a]	1.475	2.060	2.800	...
0.960	1.570	2.240	2.980	...
1.000[a]	1.640	2.360	3.100	...

Mole fraction acetone x_A	$D_{AB} \times 10^5$, cm²/sec 25°C	35°C	45°C	55°C
	Acetone-water			
0.000[a]	1.300	1.600	1.820	2.140
0.024	1.140	1.405	1.590	1.880
0.100[a]	0.810	0.990	1.120	1.350
0.142	0.720	0.860	0.990	1.180
0.200[a]	0.665	0.780	0.910	1.070
0.280	0.650	0.760	0.900	1.050
0.300[a]	0.650	0.780	0.910	1.060
0.400[a]	0.690	0.858	1.040	1.230
0.482	0.790	0.980	1.250	1.450
0.500[a]	0.820	1.025	1.290	1.510
0.600[a]	0.130	1.365	1.640	1.940
0.640	1.320	1.540	1.820	2.170
0.700[a]	1.680	1.898	2.170	2.600
0.782	2.280	2.520	2.810	3.330
0.800[a]	2.440	2.700	2.990	3.540
0.900[a]	3.560	3.900	4.310	4.990
0.944	4.220	4.550	5.400	5.720
1.000[a]	5.220	5.600	6.050	6.700
	65°C	75°C	85°C	...
0.000	...	...	...	...
0.024	2.200	2.470	2.990	...

Mole fraction acetone x_A	$D_{AB} \times 10^5$, cm²/sec 25°C	40°C	55°C
	Acetone-chloroform		
0.000[a]	2.330	2.880	3.470
0.050	2.510	3.110	3.720
0.100[a]	2.685	3.300	3.965
0.200[a]	2.926	3.624	4.355
0.245	3.020	3.740	4.490
0.300[a]	3.110	3.880	4.620
0.400[a]	3.260	4.060	4.779
0.480	3.340	4.150	4.850
0.500[a]	3.338	4.160	4.861
0.600[a]	3.448	4.212	4.932
0.685	3.505	4.240	4.970
0.700[a]	3.500	4.248	4.988
0.800[a]	3.572	4.282	5.010
0.900[a]	3.582	4.301	5.020
0.950	3.600	4.310	5.020
1.000[a]	3.620	4.320	5.030

[a] By extrapolation or interpolation of the experimental coefficients.

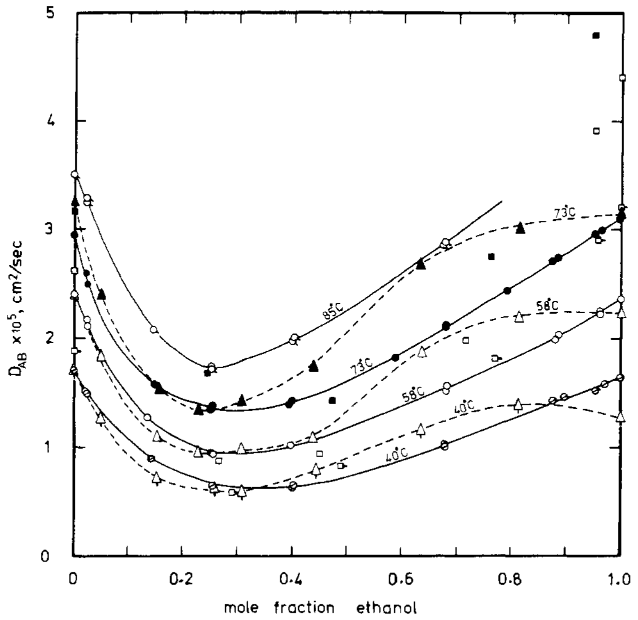

Figure 2. Differential diffusion coefficients for ethanol–water system compared with data of other authors

T, °C	This work	P-W (19)	S-S (25)
40	⊘	△	☐
58	○	△	□
73	●	▲	■
85	○		

—— This work
------ P-W (19)

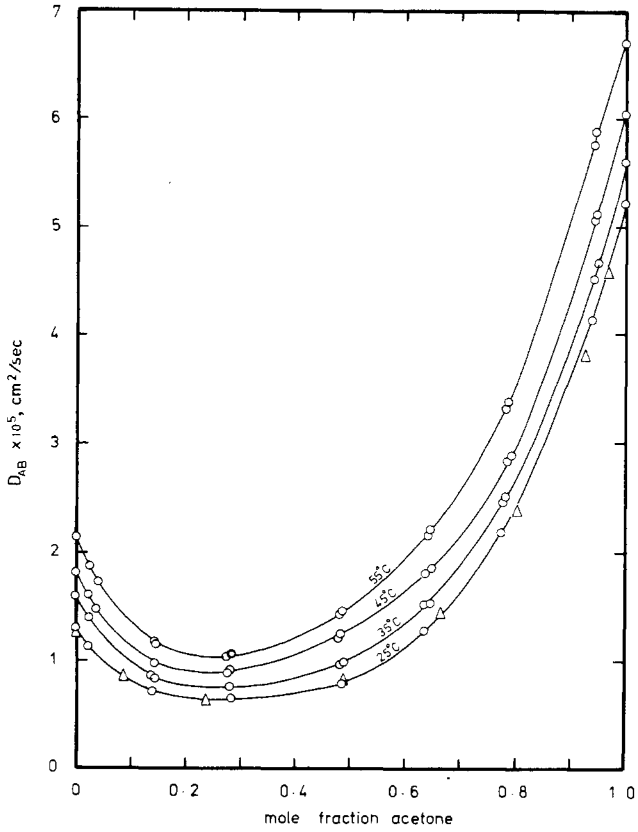

Figure 3. Differential diffusion coefficients for acetone–water system compared with data of other authors

○ This work
△ Anderson et al. (1)

ing systems. Similar limitations are put by Vignes (32) on his correlation. According to these restrictions, only the acetone–chloroform system, which is mildly associating, is suitable for testing these correlations. In this investigation, however, the other two systems (ethanol–water and acetone–water) are tested to see the extent of the effect the association has on the predictive properties of each of the equations. The Leffler and Cullinan equation is

$$D_{AB} = [D_{BA}{}^{\circ}\mu_A]^{x_A}\,[D_{AB}{}^{\circ}\mu_B]^{x_B}\,\frac{\alpha_A}{\mu_{AB}} \qquad (3)$$

and that of Vignes is

$$D_{AB} = [D_{BA}{}^{\circ}]^{x_A}\,[D_{AB}{}^{\circ}]^{x_B}\,\alpha_A \qquad (4)$$

A graphical method has been adopted for comparison of the predicted values with experimental values. Figures 5a, 5b, 6a, 6b, and 7 represent the experimental and the predicted diffusion coefficients.

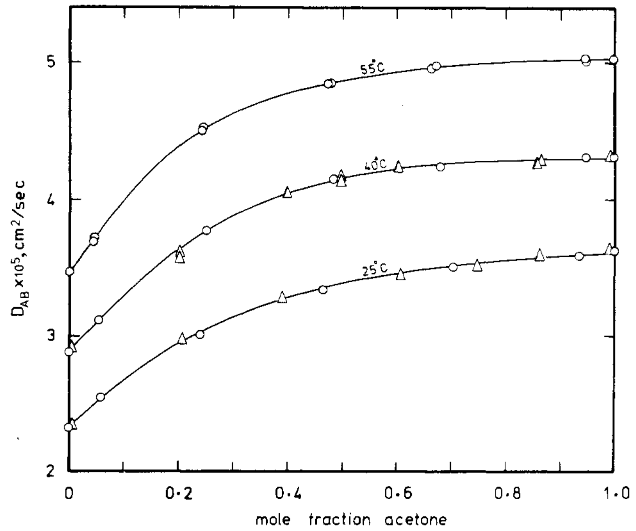

Figure 4. Differential diffusion coefficients for acetone–chloroform system compared with data of other authors

○ This work
△ Anderson et al. (1)

Table IV. Differential Diffusion Coefficients at Normal Boiling Points Obtained by Extrapolation of Experimental Data ($D_{AB} \times 10^5$ cm²/sec)

Mole fraction	Ethanol(A)–water(B)		Acetone(A)–water(B)		Acetone(A)–chloroform(B)	
x_A	T, °C[a]	D_{AB}	T, °C[b]	D_{AB}	T, °C[c]	D_{AB}
0.0	100.00	4.32	100.00	3.86	61.50	3.75
0.1	86.40	2.50	66.72	1.60	62.60	4.34
0.2	83.20	1.75	62.20	1.18	63.60	4.85
0.3	81.70	1.61	61.00	1.14	63.80	5.05
0.4	80.80	1.76	60.40	1.35	64.32	5.23
0.5	80.00	2.05	59.80	1.69	63.55	5.26
0.6	79.50	2.20	59.30	2.06	62.50	5.28
0.7	79.20	2.45	58.80	2.76	61.15	5.28
0.8	78.80	2.69	58.20	3.70	59.50	5.25
0.9	78.50	2.97	57.40	5.13	57.76	5.20
1.0	78.50	3.33	56.20	6.79	56.20	5.16

[a] Boiling points from Smith and Storrow (25). [b] Boiling points from Thomas and McAllister (28). [c] Boiling points from Reinder and Minjer (1947) taken from ref. 29.

The Leffler and Cullinan equation consistently underpredicts the coefficients for the system ethanol-water at all temperatures, the average of the deviations being −30%. The Vignes equation mostly overpredicts for this system, except for the 73°C isotherm for which the predicted values are lower, the mean deviation being approximately 13%.

In the case of the system acetone-water, Equations 3 and 4 mostly underpredict, the mean deviation for the Leffler and Cullinan equation being 29% and for the Vignes equation 14%.

The agreement of the acetone-chloroform data with the predicted values was expected, on the theoretical grounds, to be considerably better. In fact, the Leffler

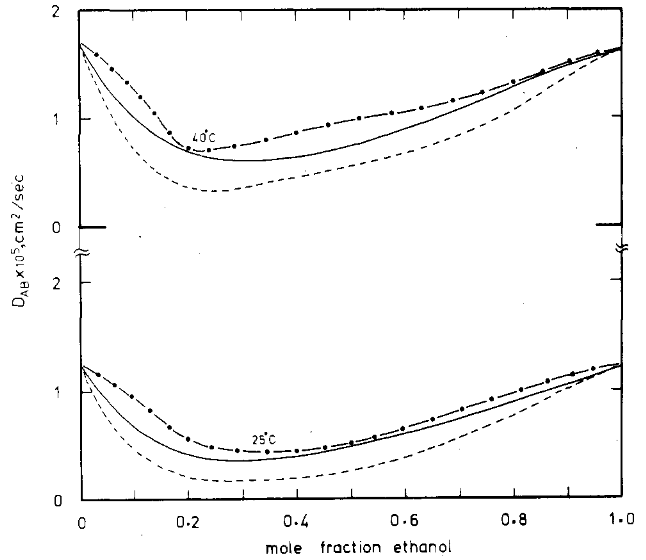

Figure 5a. Differential diffusion coefficients for ethanol-water system compared with predicted values at 25° and 40°C
—— Experimental, from Table III
- - - - Leffler and Cullinan Equation 3
– • – • Vignes Equation 4

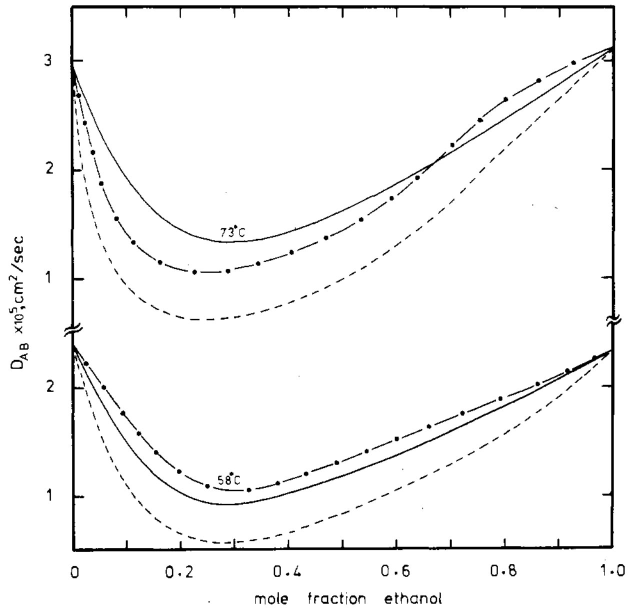

Figure 5b. Differential diffusion coefficients for ethanol-water system compared with predicted values at 58° and 73°C
—— Experimental, from Table III
- - - - Leffler and Cullinan Equation 3
– • – • Vignes Equation 4

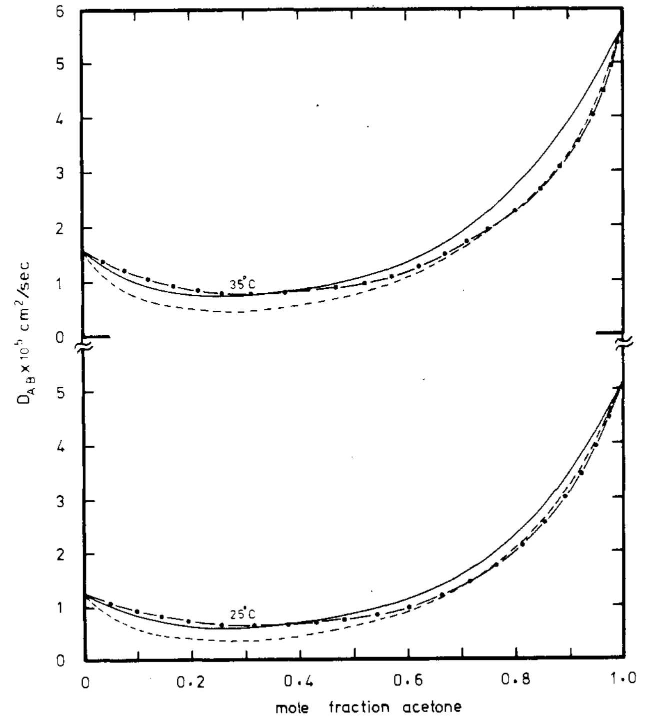

Figure 6a. Differential diffusion coefficients for acetone-water system compared with predicted values at 25° and 35°C
—— Experimental, from Table III
- - - - Leffler and Cullinan Equation 3
– • – • Vignes Equation 4

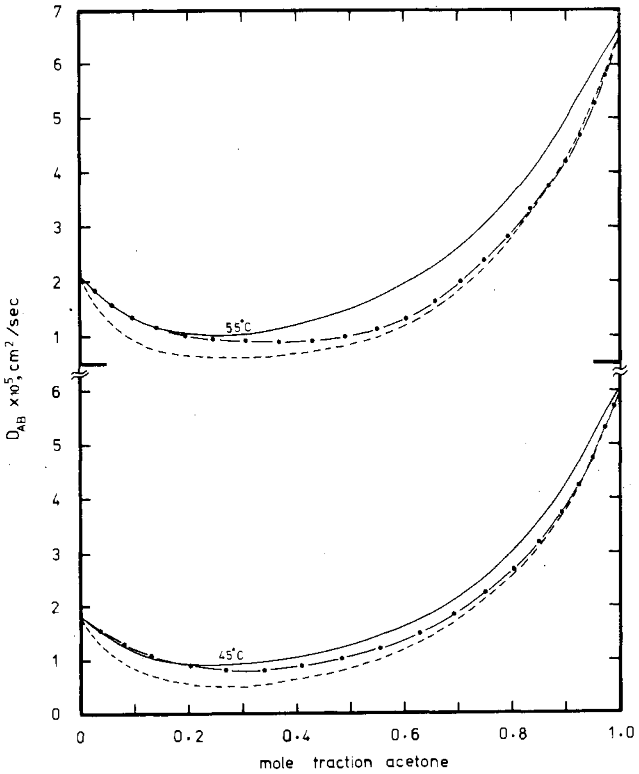

Figure 6b. Differential diffusion coefficients for acetone-water system compared with predicted values at 45° and 55°C
—— Experimental, from Table III
- - - - Leffler and Cullinan Equation 3
– • – • Vignes Equation 4

and Cullinan equation gave a mean deviation of 4.6%, whereas the mean deviation for the Vignes equation is 13.4%.

Thus, on the basis of these three binary systems, the Vignes (*32*) equation appears not to be affected by the nature of the system. The Leffler and Cullinan (*14*) equation, on the other hand, gives much poorer predictions for the associating systems (ethanol-water and acetone-water).

The diffusion coefficients at the terminal concentrations reported in Tables II and III were used to test the following three prediction equations selected from the literature:

Wilke-Chang (*34*) equation:

$$D_{AB}^{\circ} = 7.4 \times 10^{-8} \frac{(x_B M_B)^{1/2}}{\mu_B V_A^{0.6}} T \qquad (5)$$

Sitaraman et al. (*24*) equation:

$$D_{AB}^{\circ} = 5.4 \times 10^{-8} \left[\frac{M_B^{1/2} (\Delta L_B)^{1/3} T}{\mu_B V_A^{0.5} (\Delta L_A)^{0.3}} \right]^{0.93} \qquad (6)$$

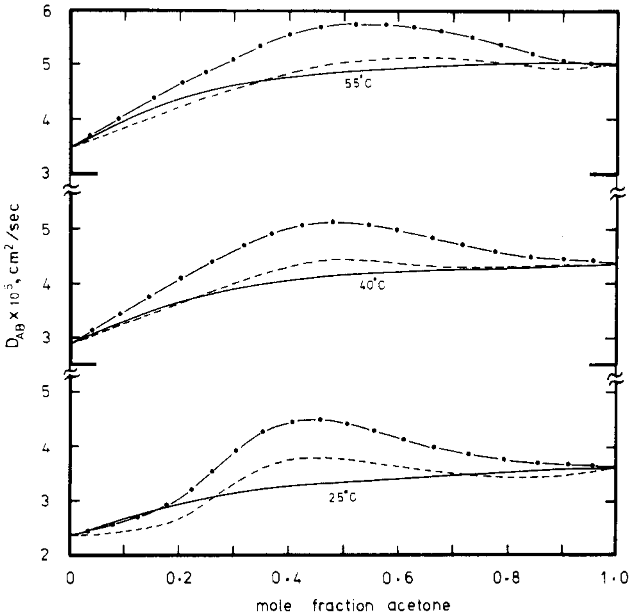

Figure 7. Differential diffusion coefficients for acetone-chloroform system compared with predicted values at 25°, 40°, and 55°C

—— Experimental, from Table III
- - - - Leffler and Cullinan Equation 3
– • – • Vignes Equation 4

Table V. Average Deviations of Predicted from Experimental Diffusion Coefficients at Infinite Dilution

Binary system		% Av deviation in predicted D_{AB}°			
Solute (A)	Solvent (B)	Tyn-Calus, Eq. 8	Wilke-Chang, Eq. 5	King et al., Eq. 7	Sitaram et al., Eq. 6
Ethanol	Water	12.9	29.7	7.8	11.2
Water	Ethanol	8.5	13.1	21.8	10.2
Acetone	Water	11.2	19.7	25.2	5.5
Water	Acetone	2.4	12.5	7.5	16.7
Acetone	Chloroform	3.9	36.7	2.5	11.5
Chloroform	Acetone	9.0	6.0	17.9	6.0

King et al. (*13*) equation:

$$D_{AB}^{\circ} = 4.4 \times 10^{-8} \left(\frac{V_B}{V_A}\right)^{1/6} \left(\frac{\Delta H_B}{\Delta H_A}\right)^{1/2} \frac{T}{\mu_B} \qquad (7)$$

These authors (*31*):

$$D_{AB}^{\circ} = 8.93 \times 10^{-8} \frac{V_A^{1/6}}{V_B^{1/3}} \left(\frac{[P_B]}{[P_A]}\right)^{0.6} \frac{T}{\mu_B} \qquad (8)$$

The detailed deviations of the predicted coefficients, for each isotherm, from the experimental values are reported (*30*). Table V gives only the average deviations of all the isotherms for each binary system. Inspection of Table V shows that Equations 5-8 predict diffusion coefficients at infinite dilution with about the same accuracy for the associating and nonassociating systems. The four equations give predictions of about the same accuracy, which is very low, as may be deduced from Table V.

Nitrogen was used in the experimental work to exert pressure on the test liquids and so to prevent boiling. Nitrogen was selected for its chemical inertness, but it has a finite solubility in test liquids, and the possibility of some interference with the diffusion process should not be excluded. The construction of the diffusion cell, Figure 1, ensures that the interfacial area between the liquid and the gas phases is very small and the interfaces are very far from the diaphragm in which the diffusion process takes place. These constructional features considerably reduce the danger of nitrogen interference. Comparison of our experimental results with those of other authors confirms the suggestion that nitrogen interference, if it existed, did not play any significant part. The method of Pratt and Wakeham (*19*) does not involve the use of any inert gas, but, as may be seen in Figure 2, our own results do not show any consistent deviation that could be ascribed to nitrogen solubility. Neither does the method of Mach Zender diffusiometer (*2*), used by Anderson et al. (*1*) to obtain diffusion coefficients for the system acetone-chloroform at 25° and 40°C, employ inert gases, but their results agree very closely with our own as illustrated in Figure 4.

However, as a further development of our diffusion cell method, a modification, to eliminate the use of inert gases, should be attempted.

Nomenclature

C_1 = initial concentration in the lower compartment, g solute/cm³ at T
C_2 = initial concentration in the upper compartment, g solute/cm³ at T
C_3 = final concentration in the lower compartment, g solute/cm³ at T
C_4 = final concentration in the upper compartment, g solute/cm³ at T
D_{AB} = differential diffusion coefficient, cm²/sec
$\bar{D}_{AB}$ = integral diffusion coefficient, cm²/sec
D_{AB}° = diffusion coefficient at $x_A \rightarrow 0$, cm²/sec
D_{BA}° = diffusion coefficient at $x_A \rightarrow 1$, cm²/sec
ΔH_A, ΔH_B = latent heats of vaporization of pure liquids A and B, respectively, at their normal boiling points, cal/g mol
ΔL_A, ΔL_B = latent heats of vaporization of pure liquids A and B, respectively, at their normal boiling points, cal/g
M_B = molecular weight of B
$[P_A]$, $[P_B]$ = parachors of pure liquids A and B, respectively, $g^{1/4}$ cm³/g mol sec$^{1/2}$
t = time, sec
T = absolute temperature, K

V_A, V_B = molal volumes of A and B, respectively, at their normal boiling points, cm^3/g mol
x_A, x_B = mole fractions of A and B in binary mixtures
X_B = association factor of the solvent B in Equation 5 ($X_B = 1$ for acetone and chloroform, 2.6 for water, and 1.5 for ethanol)
μ_A, μ_B = viscosity of pure liquids A and B, respectively; centipoises in Equations 5-8; poises in Equation 3
μ_{AB} = viscosity of binary mixture, poises
β = cell constant in Equation 1, cm^{-2}
ρ_{AB} = density of binary mixture, g/cm^3
$\alpha_A = 1 + (\partial \ln \gamma_A / \partial \ln x_A)$, thermodynamic factor
γ_A = activity coefficient

Subscripts

A = solute
B = solvent
AB = binary mixture of A and B

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Received for review October 25, 1974. Accepted March 25, 1975. The primary experimental data and the physical properties needed in processing them may be found in ref. *30*, which is available on loan from the Library of the Loughborough University of Technology.

Supplementary Material Available. The Appendix, containing tables of physical properties and primary experimental data from ref. *30*, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JCED-75-310.

Vapor Pressure-Temperature-Concentration Relationship for System Lithium Bromide and Water (40–70% Lithium Bromide)

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The vapor pressure of water over solutions containing 40, 50, 60, and 70 wt % lithium bromide was determined by direct static and gas transport methods. The data were fitted to the straight line relationship: Log $P_{(soln)} = B \text{ Log } P_{(water)} + C$, where constants B and C are concentration dependent.

Accurate vapor-pressure data for aqueous lithium bromide solutions are necessary for developing and extending the performance range of absorption air conditioning machines (*1*). There are available in the literature vapor pressure-temperature-concentration diagrams for the system LiBr–H_2O; however, these *PTX* diagrams are constructed by extrapolating small sets of data determined over narrow temperature ranges (2–4, *7*, *8*). Hence, the smoothed values given by Uemura and Hasaba (*9*) over the range 34–65% LiBr and 20–160°C are not in complete agreement with Pennington's extrapolated values (*8*), especially at temperature and concentration extremes. The vapor-pressure values presented most likely lack correlation because generalized equations derived to represent data of a nonideal salt solution are extrapolated beyond experimental data limits.

This investigation was undertaken to determine the vapor pressure of aqueous lithium bromide solutions as a function of temperature at four concentrations to increase the degree of data reliability at temperature extremes. The two simplest and most direct procedures chosen for this study are the gas transport and static methods. Results obtained by these two methods were consistent to within ±1.9%.

Experimental

General. A number of methods for measuring the vapor pressure of aqueous lithium bromide solutions were consid-

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