Table II. pK_{sp} of the Rare-Earth 8-Quinolinolates

rare earth	pK_{sp}	rare earth	pK_{sp}
Sc	34.52 ± 0.11	Tb	32.09 ± 0.23
Y	32.64 ± 0.18	Dy	32.38 ± 0.40
La	28.06 ± 0.09	Ho	31.89 ± 0.32
Pr	29.59 ± 0.45	Er	32.50 ± 0.36
Nd	30.50 ± 0.62	Tm	33.03 ± 0.85
Sm	30.80 ± 0.65	Yb	32.60 ± 1.12
Eu	31.39 ± 0.33	Lu	33.46 ± 0.60
Gd	31.38 ± 0.45		

The fact that the solubility of the rare-earth 8-quinolinates is so low, ~10^{-9} M, means that saturated solutions of only the pure rare-earth 8-quinolinate and pure water are approaching infinite dilution. This means that the activity product and the solubility product are essentially the same value. These values are given in Table II.

The molar solubilities were calculated from the solubility products and are given in Figure 1. This curve is characteristic of other rare-earth solubility curves given in the chemical literature. A "gadolinium break" is present, and the yttrium solubility coincides with the heavy-rare-earth solubility. Both features are typical of similar rare-earth curves.

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Diffusion Coefficients for the Liquid System Acetone–Cyclohexane at 298.15 K

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The diaphragm cell technique has been used to measure mutual diffusion coefficients for the system acetone–cyclohexane at 298.15 K over the complete composition range. The obtained diffusivities have been compared with the results predicted by the correlations of Sanchez and Clifton, Rathbun and Babb, and Haluska and Colver. The corresponding absolute mean deviations are computed as 1.32%, 3.77%, and 28.33%.

Introduction

Liquid-phase diffusion coefficients are important data from the fundamental as well as the practical point of view. During a mass-transfer study, the composition dependence of the diffusion coefficients is essential. This information is particularly needed for a proper design and rational operation of the separation process equipment.

Diffusion coefficients can be obtained either from experimental measurements or from the existing theoretical or empirical prediction correlations. A number of these models, applicable to nearly ideal and nonassociating systems, have been proposed in the literature (*2*, *4*, *5*, *9*, *14*, *29*). Correlations, intended to be applied to the nonideal systems and to the systems containing associated constituents, are scarce (*8*, *20*, *23*).

Since the predictive abilities of some models, cited above, are far from satisfactory, and since the others have to be more fully tested, a necessity for further experimental measurements exists. Furthermore, permanent experimental studies represent an important help in developing new theories for better describing the diffusion mechanism.

The present article reports the experimentally obtained diffusion coefficients for the binary system acetone–cyclohexane at 298.15 K through the entire range of composition. The obtained data have been compared with the values predicted by the correlations of Haluska and Colver (*8*), Rathbun and Babb (*20*), and Sanchez and Clifton (*23*). These models have been selected according to the existing information on the behavior of the investigated binary system (*3*, *17*, *19*).

Table I. Densities and Refractive Indexes of Purified Compounds at 298.15 K

	density, g cm^{-3}		refractive index	
compd	exptl	lit.	exptl	lit.
acetone	0.785 12	0.785 01 (*28*) 0.785 07 0.785 08	1.3556	1.355 99 (*28*) 1.356 09
cyclohexane	0.773 88	0.773 87 (*1*)	1.4231	1.423 54 (*1*)

Experimental Section

Chemicals. Analytical-grade acetone supplied by Merck and "RP" cyclohexane purchased from Carlo Erba, used in this work, have been further purified as described previously (*19*). Reagent-grade potassium chloride (Merck), purified as proposed by Kruis (*13*), and double-distilled water have been used to determine the diaphragm cell constant and the volumes of the cell compartments. All solutions have been prepared by weight, using a Mettler balance type H-20 and a mixing cell designed specially to minimize evaporation during weighing. Some physical properties of the purified chemicals are compared with selected published values in Table I.

Analysis. The concentration differences of the potassium chloride between the samples have been determined by a Carl Zeiss interferometer type LI 3 with a resolution of 2 × 10^{-6} R.I. units.

Composition of the acetone–cyclohexane solutions, used in the diffusion experiments, have been obtained from density measurements by means of an oscillator-type densimeter (DMA 02C, Anton Paar) (*25*). The density-composition curve for this system at 298.15 K shows a minimum at ~0.37 mole fraction of acetone. Hence, in the range 0.25–0.55 mole fraction of acetone the composition has been obtained from refractive-index measurements at 298.15 K, using a Carl Zeiss Abbe

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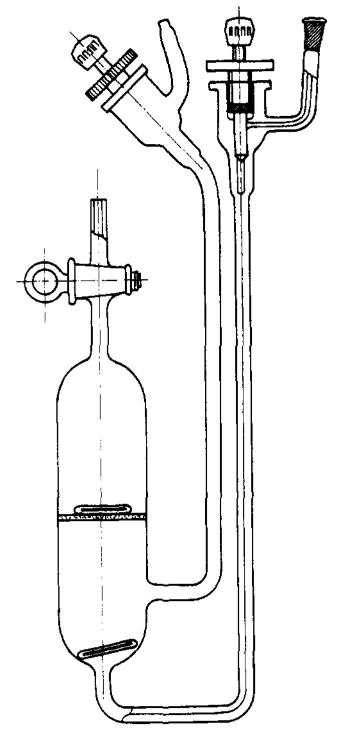

Figure 1. The diaphragm diffusion cell.

refractometer with a resolution of 0.0001 R.I. units.

Apparatus and Procedure. Because of its apparative simplicity and its high accuracy, the diaphragm cell technique has been accepted to measure diffusion coefficients of the investigated system. Two cells of Duran 50 glass (Figure 1), similar to that used by Dullien and Shemilt (*6*), have been employed. The volume of each compartment was ~25 mL, differing not more than 0.327 ± 0.002 mL. The lengths of two capillary tubes (0.5 mm i.d.), attached to the bottom compartment, were ca. 23 and 16 cm, respectively. Horizontal, 3-mm thick sintered-glass diaphragms of porosity 4, manufactured by Jobling Co., and having a pore size in the range 5–15 μm, were used. Stirring of the liquid in the compartments has been performed by two soft iron bars, sealed in thin-walled glass tubings, as suggested by Stokes (*26*), rotating at ~120 rpm by means of permanent U-shaped magnets.

The cells have been calibrated at 298.15 K by using 0.45 M potassium chloride solutions, diffusing from the lower compartment into pure water. In the calibration procedure the prerun period has been eliminated as stated by Holmes (*10*) and confirmed experimentally by Mills et al. (*18*). Following the conclusion of the latter authors concerning the calibration runs, the lower compartment and the diaphragm were initially filled with the solution. In calculating the cell constant, we have used eq 1 in conjunction with the diaphragm cell integral diffusion

$$\bar{D} = \frac{1}{\beta t} \ln \frac{c_{i,B} - c_{i,T}}{c_{f,B} - c_{f,T}} \tag{1}$$

coefficients for the potassium chloride–water system, reported by Woolf and Tilley (*31*). The obtained values for cell constants and for the corresponding 95% confidence intervals are β(cell I) = 0.1941 ± 0.0026 and β(cell II) = 0.2540 ± 0.0033. These values refer to the six and five calibration runs for cells I and II, respectively.

The cell constants were determined in the course of the experiments. There was no detectable trend of the cell constants within the total time of the runs.

Table II. Experimental Integral Diffusion Coefficients for the System Acetone–Cyclohexane at 298.15 K

x_1	$10^5\bar{D}_{12}$, cm^2 s^{-1}	x_1	$10^5\bar{D}_{12}$, cm^2 s^{-1}	x_1	$10^5\bar{D}_{12}$, cm^2 s^{-1}
0.0000	2.22[a]	0.2995	1.34	0.9500	3.49
0.0193	2.05	0.4507	1.48	0.9813	3.71
0.0494	1.84	0.5993	1.72	1.0000	4.06[a]
0.1132	1.61	0.8077	2.39		

[a] Values obtained by graphical extrapolation of the experimental diffusivity–composition results.

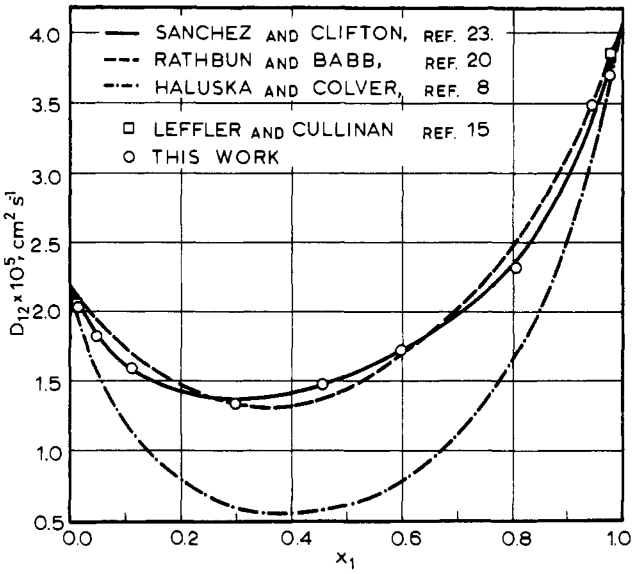

Figure 2. Experimental integral diffusion coefficients for the acetone–cyclohexane system at 298.15 K compared with the predicted values.

In the diffusion runs with organic mixtures, the initial concentration distribution in the diaphragm (solution-filled diaphragm) has been the same as in the calibration procedure. The higher-density solution was always placed in the bottom compartment.

A Cannon constant-temperature bath Model M1 has been used to maintain the cells, containing the diffusing liquids, at 298.15 ± 0.01 K.

Results and Discussion

Integral diffusion coefficients have been calculated from the experimental observations by means of eq 1. Although this equation assumes constant solution volumes during the run, the results obtained for the ethanol–water system (*7*, *22*) indicate that, for experiments with small initial concentration differences, the error introduced by using eq 1 and hence neglecting the volume changes taking place on diffusion is insignificant. In view of the relatively small initial concentration differences, established in the cell during the present investigations (~0.02–0.06 mole fractions in the region of more pronounced curvature of the diffusivity–composition line, and ~0.10 mole fractions over its nearly linear part), it seems reasonable to assume that the experimental integral diffusion coefficients, reported in Table II, do not differ significantly from the differential diffusivities at the mean concentration of the experiment. Figure 2 demonstrates the good agreement of the data of Leffler and Cullinan (*15*) with the present experimental results.

Correlations, suggested in the literature (*8*, *20*, *23*), have been used to carry out the predictive calculations for the investigated system, using the thermodynamic and transport properties from various sources. The experimental viscosity data of Campbell et al. (*3*) have been fitted to eq 8 of ref *11*. The obtained equation has been used to compute the viscosity values at the mean composition of each diffusion experiment. Values of the thermodynamic factor, α (eq 2), have been

$$\alpha = 1 + (\partial \ln \gamma_1/\partial \ln x_1)_{T,P} \tag{2}$$

Table III. Diffusion Coefficients at Infinite Dilution

estimation method	$10^5 D_1^\circ$, cm^2 s^{-1}	$10^5 D_2^\circ$, cm^2 s^{-1}
Wilke-Chang (*30*)	3.34	1.72
Scheibel (*24*)	4.42	2.41
Reddy-Doraiswamy (*21*)	3.75	1.53
Lusis-Ratcliff (*16*)	3.83	1.83
King et al. (*12*)	4.09	1.56
extrapolation by the best fit of the diffusivity data to pure components	3.96	1.94
graphical extrapolation of the experimental diffusivity data to pure components	4.06	2.22

calculated from the vapor-liquid equilibrium data of Tasić et al. (*27*). The diffusion coefficients at infinite dilution are required for all predictive calculations as well. These data have been estimated by several approaches. The first was the use of various predictive correlations from the literature (*12*, *16*, *21*, *24*, *30*). The second procedure consisted of fitting the diffusivity-composition data to polynomials by a method of least squares and extrapolating the best polynomial to the end points. Finally, the limiting diffusivities have been estimated by a graphical extrapolation of the experimental curve. The obtained results are presented in Table III.

It can be seen from this table that the limiting diffusion coefficients, obtained from the selected prediction correlations and from the best empirical fitting equation, differ significantly from one method to another. Moreover, these values are far from the limiting diffusivities expected to correspond to the rest of the present experimental diffusion data. Hence, all predictive calculations have been carried out by using the limiting diffusion coefficients estimated by graphical extrapolation of the curve drawn through the experimental data points.

Diffusion coefficients, estimated by the methods of Haluska and Colver (*8*), Rathbun and Babb (*20*), and Sanchez and Clifton (*23*) have been compared with the experimentally obtained values. The corresponding absolute mean deviations, defined by eq 3, are 28.33%, 3.77%, and 1.32%, respectively.

$$E = \frac{100}{k} \sum_{i=1}^{k} \frac{|\bar{D}_{12,\mathrm{calcd}} - \bar{D}_{12,\mathrm{exptl}}|_i}{\bar{D}_{12,\mathrm{exptl}}} \qquad (3)$$

It can be noted that the correlation of Sanchez and Clifton provides the best description of the diffusion process in the investigated binary. Value of the constant *m*, from the eq 11 of ref *23*, has been calculated as $m = 0.62$. The model of Rathbun and Babb, with an optimal value of the exponent $s = 0.442$, appearing in eq 6 of ref *20*, also gave good agreement with the experiments. On contrary, the correlation of Haluska and Colver considerably underpredicts the diffusivities at all compositions, and hence it is not suitable for the present use.

Glossary

c	molar concentration, g-mol cm^{-3}
$\bar{D}$	integral diffusion coefficient, cm^2 s^{-1}
E	absolute mean deviation, defined by eq 2
k	number of data points
T	absolute temperature, K
x	mole fraction
t	time, s

Greek Letters

α	thermodynamic factor
β	cell constant, cm^{-2}
γ	activity coefficient

Subscripts

B	bottom compartment
f	final conditions
i	initial conditions
T	top compartments
1	acetone
2	cyclohexane
exptl	experimental value
calcd	calculated value

Superscripts

0	infinite dilution

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