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Ethylene Solubility and Diffusivity in Hexane–Dodecane and Ethylene Glycol–Butanol Solutions

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Densities, refractive indices, viscosities, ethylene solubilities, and diffusion coefficients all at 25 °C are reported for the solvent solutions composed of hexane–dodecane and butanol–ethylene glycol. In the first of these two solvent solutions both components were nonpolar whereas in the second both were polar and expected to form hydrogen-bonding association complexes in solution. A comparison of the various solution properties for these two types of solutions was found useful. The data were also compared with previously reported results when available and predicted values utilizing empirical equations when applicable.

Introduction

A knowledge of the solution properties for mixed solvents of two (or more) components is frequently required in the chemical processing industry. These properties may include the density, viscosity, or gas solubility and diffusivity, as well as refractive index for possible solution analysis, among others. Relatively few data are available for gas solubilities and diffusion coefficients in mixed solvents. In this work the above-mentioned solution properties, as well as ethylene solubilities and diffusivities are reported at 25 °C both for nonpolar solvent solutions composed of hexane and dodecane and for solutions composed of the polar liquids butanol and ethylene glycol.

The subject of liquid diffusion in nonelectrolytes has been extensively reviewed in two parts by Ghai et al. (*9*, *10*) with regard to most aspects of diffusion including measurement techniques, theoretical considerations, and predictive equations. The particular subject of diffusivities of dissolved gases was reviewed earlier by Himmelblau (*17*). The Wilke–Chang relation (*32*) for predicting diffusivities in liquids including those for dissolved gases has stood the test of time, although two significant limitations for its use have been observed by Akgerman and Gainer (*1*). Diffusivities of small solute gas molecules were not usually accurately predicted nor were those involving solvents whose viscosities were greater than 3–5 cP. The latter authors developed a correlation (*1*, *2*) for diffusivities of dissolved gases based on the absolute rate theory which they showed to be a significant improvement over the Wilke–Chang correlation although also more complex:

$$D_{AB} = \frac{kT}{\xi_A \mu_B}\left(\frac{N}{V_B}\right)^{1/3}\left(\frac{M_B}{M_A}\right)^{1/2} \exp\left(\frac{E_{\mu B} - E_{DAB}}{RT}\right) \quad (1)$$

$$E_{\mu B} - E_{DAB} = E_{BB}^{j}\{1 - (E_{AA}^{j}/E_{BB}^{j})^{1/(\xi_A+1)}\} \quad (2)$$

$$\xi_A = 6(V_A/V_B)^{1/6} \quad (3)$$

The work of the original authors should be consulted for methods of calculating the various activation energies and other parameters.

The diffusivity of a gas in a mixed solvent solution composed of two liquids may be considered to involve a pseudobinary system since the gas component is usually very dilute. A number of methods have been proposed to describe the diffusivity of a dilute species in mixed solvents as discussed by Himmelblau in his review (*17*). More recently Tang and Himmelblau (*28*) and Leffler and Cullinan (*20*) have addressed this problem. Several possible relations were described by the former authors, none of which was clearly superior in representing the diffusivity of toluene and CO_2 in several mixed solvent solutions; however, the relation best able to represent the data is as follows:

$$D_{1M}(\eta_M)^{1/2} = x_2 D_{12}(\eta_2)^{1/2} + x_3 D_{13}(\eta_3)^{1/2} \quad (4)$$

From a basis of the Vignes equation (*31*) Leffler and Cullinan developed an equation for the concentration dependence of the diffusivity of a dilute species in a mixture of two solvents as follows:

$$(\lim_{x_1 \to 0} D_{1M})\,\eta = (D^\circ{}_{12}\eta_2)^{x_2}(D^\circ{}_{13}\eta_3)^{x_3} \quad (5)$$

Equation 5 was not specifically tested for gaseous solutes nor for highly polar solvent mixtures; hence its application to such systems is uncertain. An empirical expression for the relation between diffusivity of a dilute solute in a number of solvents or mixed solvent solutions was reported by Hayduk and Cheng (*14*).

$$D^\circ{}_{AB}\eta^{A} = B \quad (6)$$

Equation 6 could be applied to gaseous solutes but was not expected to apply when the solvents or solvent solutions were strongly associating.

Other properties which are usually required for the determination and correlation of gas diffusivities in mixed solvents include the gas solubility, solution viscosity and density for the solvent solutions. In addition it is necessary to have a method of analysis for the solvent compositions, usually by means of refractive index measurements. Theoretical aspects of gas solubilities in mixed solvents have been recently discussed by

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a number of workers (*23*, *29*). Predictions of gas solubilities in mixed solvents, particularly for those forming highly nonideal solutions, have been only partially successful. The subject of volume changes on mixing for binary liquid mixtures has been reviewed by Battino (*6*). It is of interest that solution densities of two mixed liquids, or equivalently the excess volume of mixing, is often written as a function of the solution concentration in mole fraction of one of the components. As indicated by Mikhailov (*22*) there is an advantage in expressing two-component solution densities in terms of the volume fraction based on the volumes of components prior to mixing.

$$z_k = n_k \tilde{V}_k^\circ / \sum_i n_i \tilde{V}_i^\circ \qquad (7)$$

As discussed by Battino, three similar but not identical volume fractions may be defined. The relation between density and composition as defined by eq 7 then becomes linear for ideal solutions involving no volume changes on mixing. Where the component molar volumes are significantly different, however, the relation between density and composition expressed in mole fraction would be no longer linear. It would appear that certain solution properties such as density could best be related to compositions expressed as volume fractions, certain others such as vapor pressure and generally other colligative properties to compositions expressed in mole fractions, and still other properties such as viscosity could be simply related to neither of the two common methods for expressing concentration.

Experimental Section

Diffusion coefficients of ethylene were measured by using the steady-state capillary cell method described previously (*11*, *16*, *21*). Each cell was constructed with two sizes of precision bore glass capillary tubing joined together. The lower portion of 0.1016 ± 0.0005 cm diameter confined the diffusion system while the upper portion of 0.0406 ± 0.0005 cm diameter was used for gas volume measurements. During deaeration the concentration of the solvent solution was usually altered; hence it was necessary to sample the deaerated solutions for analysis by measurement of refractive index. A period of up to 30 h in the constant-temperature bath controlled to ±0.01 °C was required for the most viscous solvent prior to the actual absorption rate measurement, to ensure that a steady-state concentration profile was established in the liquid confined in the capillary. The cells were firmly supported by rods fastened to a frame completely separate from the bath itself, in that way minimizing possible effects of mechanical vibration. One experiment took up to 4 days to complete, particularly for ethylene glycol solvent. To reduce the duration of the experiments several cells were used simultaneously. Because of their hygroscopic nature aqueous ethylene glycol solutions were prepared minimizing exposure to the air using freshly opened glycol having a specified maximum water content of 0.2 wt %. Immediately after preparation the solutions were charged into the deaerating apparatus and subsequently directly into a gastight syringe for solubility measurement, or a diffusion cell for diffusion measurement, thus avoiding any further exposure to the air.

Diffusivities were calculated from a knowledge of the gas absorption rate, utilizing the saturated solubility at the prevailing barometric pressure, the length of the diffusion path, and the relative sizes of the two capillaries. Diffusivities of ethylene in hexane-hexadecane solutions were based on a mathematical model for liquids of constant mass concentration along the diffusion path (*21*).

$$D = n_A l / \rho_A \ln \left\{ \frac{1 + K\omega_{AO}}{1 + K\omega_{AL}} \right\} \qquad (8)$$

Diffusivities of ethylene in butanol-glycol solutions were calculated on the basis of the assumption of constant molar concentration along the diffusion path.

$$D = N_A l V_A / \ln \left\{ \frac{1 + K' x_{AO}}{1 + K' x_{AL}} \right\} \qquad (9)$$

It was determined that of the two methods of expressing concentration, the assumption of constant mass concentration was more valid for the hydrocarbon solutions, while the assumption of constant molar concentration was more valid for solutions composed of ethylene, butanol, and ethylene glycol. Simplified forms of eq 8 and 9 which were based on the assumption that any ethylene passing through the confined liquid did not occupy any space were found to give nearly equivalent results.

$$D = n_A l / \rho(\omega_{AO} - \omega_{AL}) \qquad (10)$$

$$D = N_A l / C(x_{AO} - x_{AL}) \qquad (11)$$

Saturated solubilities of ethylene at atmospheric pressure were obtained from the related graph of solubility vs. composition of solvent and corrected to the prevailing ethylene partial pressure. It was found that the volume change of the gas confined above the liquid through which the gas was diffusing was essentially independent of pressure. The molar volume of dissolved ethylene was taken to be constant in all solutions at 60.4 cm^3 at 25 °C, an average value obtained from the coefficients of dilation for ethylene dissolved in a number of solvents as reported by Horiuti (*18*) which is similar to that reported by Ribeiro et al. (*24*). Corrections for the small amount of gas initially present in the liquid were also made. The effective solute diffusivity was considered to remain constant along the diffusion path. Hence the diffusivities obtained may be considered to be integral average values corresponding to the average solute concentration along the diffusion path. Because of the relatively low average ethylene concentration employed (<2.2 mol %), the diffusivities may be considered to be equivalent to diffusivities at infinite dilution. The standard deviation of duplicate results for diffusivity measurements, reported as a percentage of the mean, was 1.8%. Hence the 95% confidence limits for a single measurement are estimated to be ±4.0%.

Ethylene solubilities were measured in the solvent solutions utilizing a solvent flow apparatus described elsewhere (*13*). The apparatus entailed a continuous flow of deaerated solvent injected into an absorption spiral by means of a calibrated syringe pump, for saturation with gas. A mercury lift device was used for continuously adjusting the residual gas volume at constant pressure. The determinations were made at 25.0 ± 0.05 °C and at atmospheric pressure. Corrections for the volumes of gas dissolved to standard pressure were made utilizing Henry's law. Samples of deaerated solvents were analyzed by refractive index to determine the actual compositions injected into the solubility apparatus. Results were usually obtained in duplicate by filling two syringes with the same composition of deaerated solvent and were reproducible yielding results the standard deviation of which was 1.4%. Hence the 95% confidence limits for a single measurement are estimated to be 3.0%.

Liquid densities were determined by means of an Anton Paar (Austria) Model DMA 02C digital precision density meter. This instrument utilized a vibrating reed, the frequency of which was closely related to the density of the fluid in which it was immersed. Calibration was accomplished with two fluids of accurately known density, such as distilled water and dried air. The calibration constant, *A*, was obtained from the fluid densities and corresponding vibration frequencies, *T*.

$$\rho_1 - \rho_2 = (1/A)(T_1^2 - T_2^2) \qquad (12)$$

The instrument yielded replicate density results which had a

Table I. Density, Refractive Index, and Viscosity of Hexane, Dodecane, Butanol, and Ethylene Glycol at 25 °C

solvent	density, g/cm^3	refractive index n^{25}_D	viscosity, cP	ref
hexane	0.6552	1.3724		this work
	0.65479	1.37226		5
	0.6550	1.3720	0.2958	7
	0.6550		0.2979	27
dodecane	0.7452	1.4195		this work
	0.7451	1.4195		30
	0.7450	1.4193	1.3379	7
	0.7454		1.3793	27
			1.378	4
butanol	0.8061	1.3973	2.584	this work
	0.8056	1.3974		30
	0.8060	1.3973		4
glycol	1.1096	1.4299		this work
	1.1098		17.01	16
	1.1099	1.4306		30

standard deviation of less than 0.0001 g/cm^3 when the temperature surrounding the measurement chamber was maintained to ±0.005 °C.

Refractive indices were measured by means of a Bausch and Lomb Abbe-3L refractometer. The standard deviation of duplicate measurements was also less than 0.0001. Solvent solutions were prepared volumetrically. Viscosities for the butanol-glycol solutions were determined by using calibrated Cannon-Fenske viscometer tubes immersed in a constant-temperature bath (±0.01 °C). The viscosity of ethylene glycol was taken from the literature because considerable precautions were normally required to ensure that water was not absorbed by this highly hygroscopic solvent, with the associated drop in viscosity (*16*).

Ethylene of the CP grade and having a specified minimum purity of 99.5 mol % was purchased from Matheson of Canada. The gas molar volume was obtained from International Thermodynamic Tables (*3*) with a value at 25 °C and atmospheric pressure corresponding to 24326 cm^3/mol. The solvents, hexane, butanol, and ethylene glycol, were obtained from Fisher Chemicals and were specified to have minimum purities of 99.0, 99.0, and 99.8 mol %, respectively. Research grade dodecane was obtained from Phillips Petroleum with a specified minimum purity of 99.0 mol %.

Results and Discussion

Densities and refractive indices at 25 °C for hexane, dodecane, butanol, and ethylene glycol are listed and compared with previously published values in Table I. Since an estimate of the 95% confidence limits for both of the above measurements is ±0.0002, the comparison with previously reported values is considered generally satisfactory. Repeated experiments with freshly opened ethylene glycol did not reproduce the slightly higher values of refractive index quoted by Timmermans (*30*), however. Except for butanol, viscosities have been obtained from literature sources. It is noted that a difference between the viscosities for dodecane as reported by Shieh and Lyons (*27*) and Bidlack and Anderson (*7*) exceeds the normal experimental error.

The densities and refractive indices at 25 °C for the solvent solutions hexane and dodecane and butanol and ethylene glycol are listed in Table II as a function of composition expressed both as mole fraction and also as volume fraction (eq 7). These data are also graphically shown in Figures 1 and 2. The densities rather than excess volumes are shown as a function of composition because the accuracy of the measurements was insufficient to give consistent excess volumes. Of the three sources of density data for hexanedodecane solutions, those of Shieh and Lyons gave the most consistent excess volumes. It may be observed that the relation between density as well

Table II. Density and Refractive Index at 25 °C for Hexane-Dodecane and Butanol-Ethylene Glycol Solutions and Viscosity for the Latter Solvent Solutions

	concn second component z_2	concn second component x_2	density, g cm^{-3}	refractive index n^{25}_D	viscosity, cP
hexane-dodecane	0.100	0.0600	0.6650	1.3790	
	0.200	0.1257	0.6748	1.3836	
	0.300	0.1978	0.6834	1.3889	
	0.400	0.2772	0.6912	1.3935	
	0.500	0.3652	0.7013	1.3985	
	0.600	0.4632	0.7089	1.4030	
	0.700	0.5731	0.7181	1.4075	
	0.900	0.8381	0.7367	1.4160	
butanol-ethylene glycol	0.100	0.1527			3.18
	0.200	0.2914	0.8660	1.4043	
	0.300	0.4133	0.8968	1.4080	
	0.400	0.5229	0.9278	1.4112	6.05
	0.500	0.6218	0.9596	1.4145	
	0.600	0.7115	0.9895	1.4181	8.75
	0.700	0.7932	1.0190	1.4210	
	0.800	0.8680	1.0520	1.4243	12.33

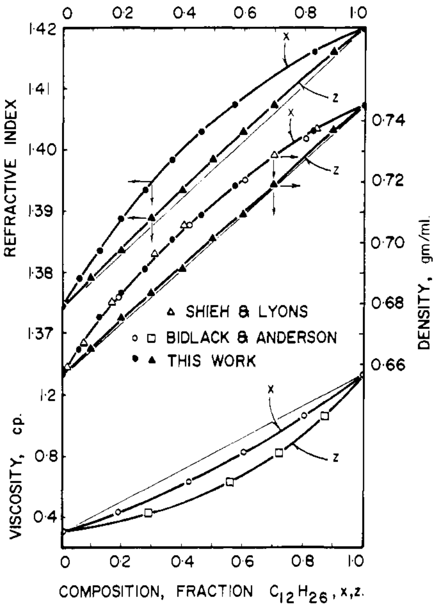

Figure 1. Refractive index, density, and viscosity at 25 °C for hexane-dodecane solutions.

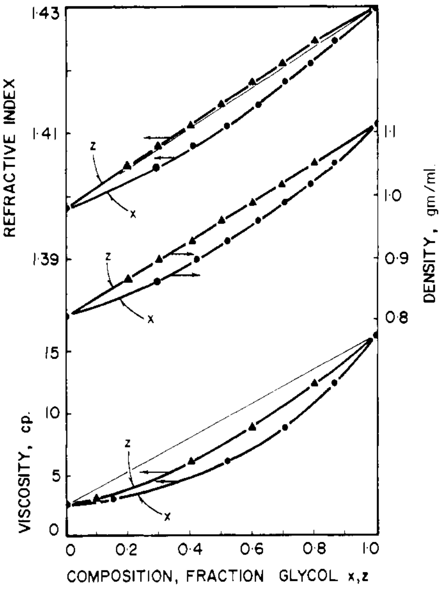

Figure 2. Refractive index, density, and viscosity at 25 °C for butanol-ethylene glycol solutions.

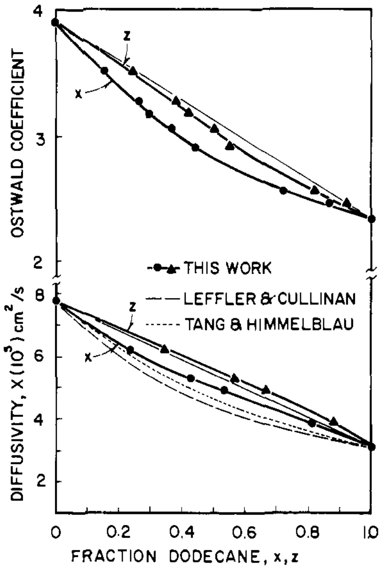

Figure 3. Ethylene solubility and diffusivity at 25 °C in hexane–dodecane solutions.

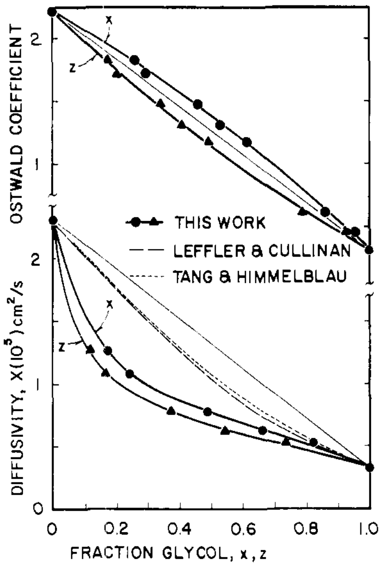

Figure 4. Ethylene solubility and diffusivity at 25 °C in butanol–ethylene glycol solutions.

as of refractive index and composition is nearly a linear function when the composition is expressed as the *volume fraction* rather than mole fraction for both solvent solutions. The viscosities for hexane–dodecane solutions at 25 °C of Bidlack and Anderson (*7*) and for butanol–ethylene glycol solutions as obtained in this work are also shown in Figures 1 and 2, respectively.

Ethylene solubilities and diffusion coefficients at 25 °C in hexane–dodecane and butanol–ethylene glycol solvent solutions are listed in Table III and illustrated in Figures 3 and 4. Ethylene solubilities in several pure nonpolar and polar solvents, including butanol and ethylene glycol, have been reported earlier (*26*). It can be observed from Figures 3 and 4 that the ethylene solubility in the hydrocarbon solvent solution is relatively constant when expressed as a mole fraction, changing a maximum of 5% over the whole composition range. On the other hand, ethylene solubilities in butanol–ethylene glycol solutions vary by a factor of approximately 12 over the whole concentration range when expressed as a mole fraction. The varying degree of hydrogen bonding in the butanol–ethylene glycol solution may be responsible for the wide variation in ethylene solubility. It may be observed that for the ethylene solubilities expressed as Ostwald coefficients, the relationship between solubility and mixed solvent composition is approximately linear when the solvent composition is expressed as a *volume fraction*. The diffusivity of ethylene in the hydrocarbon solvent solution is approximately linear with composition whereas the effect of hydrogen bonding or association in butanol–ethylene glycol solutions seems very pronounced. It would appear that the presence of even low concentrations of ethylene glycol significantly reduces ethylene diffusivity probably because of its strong associative tendency. A measure of the associating tendency may be obtained from the hydrogen-bonding factor, α_{solvent}, as defined for gas solubilities in polar solvents (*15*). The comparable hydrogen-bonding factors at 25 °C for dissolved ethylene, in order of increasing values, are: for water 0.0053, for ethylene glycol 0.0421, for butanol 0.525, and for chlorobenzene 0.723. For nonassociating solvents hydrogen-bonding factors tend to approach unity. It would appear therefore, that the associating tendency of ethylene glycol is roughly midway between that for water and butanol. Hence a significant effect of association may be expected in ethylene glycol solutions.

Table III. Ethylene Solubility and Diffusivity at 25 °C in Hexane–Dodecane and Butanol–Glycol Solutions

	concn of second component		solubility		diffusivity, cm² s⁻¹
	z_2	x_2	L	10^4x_3	(10^5)
hexane–dodecane	0	0	3.91	207	7.82
	0.241	0.155	3.51	207	
	0.351	0.238			6.18
	0.380	0.261	3.27	206	
	0.422	0.296	3.17	205	
	0.502	0.367	3.06	206	
	0.572	0.434			5.27
	0.578	0.442	2.92	205	
	0.667	0.535			4.87
	0.821	0.722	2.56	207	
	0.886	0 814			3.86
	0.922	0.871	2.47	214	
	1.0	1.0	2.35	216	3.11
butanol–glycol	0	0	2.23	83.4	2.31
	0.114	0.172			1.26
	0.163	0.239			1.08
	0.174	0.260	1.82	61.1	
	0.201	0.295	1.72	57.0	
	0.342	0.461	1.48	45.6	
	0.367	0.485			0.774
	0.407	0.531	1.31	38.4	
	0.490	0.615	1.17	33.4	
	0.542	0.658			0.623
	0.738	0.820			0.527
	0.790	0.860	0.604	15.1	
	0.927	0.956	0.450	10.6	
	1.0	1.0	0.312	7.15	0.333

The predictive equations for diffusivity of dissolved gases in mixed solvents of Leffler and Cullinan (*20*) and Tang and Himmelblau (*28*), eq 4 and 5, were tested as shown in Table IV and Figures 3 and 4. Although it is apparent that for the hydrocarbon solution the equation of Tang and Himmelblau predicted diffusivities slightly closer to the experimentally determined ones, both equations may be considered successful, with predicted values having a maximum deviation from experimentally determined ones of 11%. On the other hand, while both equations predicted similar ethylene diffusivities in butanol–ethylene glycol solutions, neither predicted the strong influence of ethylene glycol even at low concentrations. Deviations from experimentally determined diffusivities are up to 55%.

Equations 1, 2, and 3 of Akgerman and Gainer (*1*) and that of Wilke and Chang (*32*) were used to determine ethylene diffusivities in the pure solvents hexane, dodecane, butanol, and ethylene glycol as shown in Table IV. The prediction based on the Wilke–Chang equation was the more accurate for ethylene diffusivity in hexane, while both equations were somewhat less accurate in the prediction of ethylene diffusivities in dodecane.

Table IV. Comparison of Ethylene Diffusivity at 25 °C in Pure Solvents and Mixed Solvent Solutions with Predicted Values

	concn x_2	diffusivity, $cm^2\ s^{-1}$ (10^5)				
		exptl	Wilke-Chang	Akgerman-Gainer	Tang-Himmelblau	Leffler-Cullinan
hexane-dodecane	0	7.82	6.61	5.86		
	0.238	6.18			6.03	5.76
	0.434	5.27			4.98	4.71
	0.535	4.87			4.55	4.31
	0.814	3.86			3.61	3.52
	1.0	3.11	2.01	2.13		
max dev, %			35	32	7	11
butanol-glycol	0	2.31	0.87[a]	1.19		
	0.172	1.26			1.84	1.83
	0.239	1.08			1.67	1.65
	0.485	0.774			1.09	1.03
	0.658	0.623			0.774	0.730
	0.820	0.527			0.539	0.500
	1.0	0.333	0.14[b]	0.481		
max dev, %			62	48	55	53

[a] Association parameter as for ethanol. [b] Association parameter as for methanol.

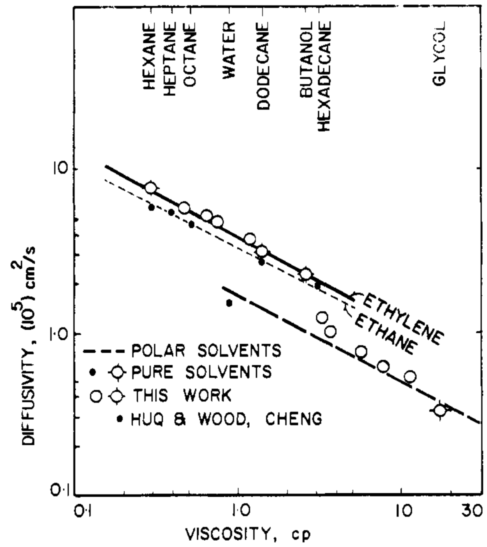

Figure 5. Diffusivity of ethylene at 25 °C in nonpolar and polar solvents and solvent solutions.

Predictions for ethylene diffusivities in the polar and/or associating solvents, butanol and ethylene glycol, were only of the correct order of magnitude. The claim by Akgerman and Gainer that their correlation was an improvement over that of Wilke and Chang especially for associating solvents was borne out by the comparison in Table IV. The substantial effect of association in the glycol-rich solvent solution is further illustrated in Figure 5 which shows ethylene and ethane diffusivities as a function of solvent viscosity. The linear relations are empirical ones as expressed by eq 6. Ethane diffusivities are from Hayduk and Cheng (*14*) while those for ethylene in water are from Huq and Wood (*19*). Ethylene diffusivities in water and glycol-rich solutions may be extrapolated and observed to be approximately *half* as large as those in nonassociating solvent solutions of the same viscosity. It may be concluded that a better knowledge of the effect of molecular association in solvent solutions is a prerequisite to more successful general correlations for diffusivity.

Ross and Hildebrand (*25*) postulated that the diffusivities of several different substances, particularly those for dissolved gases, in a single solvent depended on a characteristic molecular cross-sectional area of each substance and suggested that the value of the term $D\sigma^2$ should remain constant for such systems. The characteristic molecular area was considered to be proportional to the square of the collision diameter, σ^2. Table V shows a comparison of $D\sigma^2$ at 25 °C for the gases methane, ethane, ethylene, and propane in the solvents hexane and dodecane. Collision diameters were from the work by Flynn and Thodos (*8*). Considering the uncertainties associated with the diffusivities and the collision diameters, we find the constancy of $D\sigma^2$ is well illustrated in the two solvents. There appears to be a good basis for extrapolation of diffusivity data for dissolved gases in a particular solvent when some data are available for gases of roughly similar molecular size.

Table V. Comparison of Diffusivity of Hydrocarbon Gases at 25 °C in Hexane and Dodecane

solvent	gas	D, $cm^2\ s^{-1}$ (10^5)	σ(*8*), Å	$D\sigma^2$
hexane	methane	8.64 (*11*)	3.808	125.4
	ethylene	7.82	4.066	129.3
	ethane	5.79 (*14*)	4.384	111.3
	propane	4.48 (*12*)	5.240	123.0
dodecane	methane	3.94 (*11*)	3.808	57.2
	ethylene	3.11	4.066	51.4
	ethane	2.73 (*14*)	4.384	52.5
	propane	2.14[a]	5.240	58.8

[a] Estimated from viscosity-diffusivity relation (*12*).

Glossary

A, B	constants in eq 6, dimensionless
C	average total molar concentration along diffusion path, mol/cm³
D_{12}, D	diffusivity of 1 in 2, diffusivity, cm²/s
D°_{AB}	diffusivity of A through B at infinite dilution, cm²/s
$E_{\mu B}$	viscosity activation energy, cal/mol
E_{DAB}	diffusivity activation energy, cal/mol
k	Boltzmann constant, erg/K
K	constant in eq 8 ($=\rho/\rho_A$)
K'	constant in eq 9 ($= V_A/V$)
l	diffusion path length, cm
L	Ostwald coefficient, cm³ of gas/cm³ of solvent
M_A, M_B	molecular weights, components A, B
n_A	mass flux of component A, g/(cm² s)
N_A	molar flux component A, mol/(cm² s)
n_i, n_k	number of moles of component i, k
R	gas constant, cal/(mol K)
T	absolute temperature, K
V	molar volume of solution, cm³/mol
V_A, V_B	molar volume components A, B, cm³/mol
$\bar{V}_i^\circ$, $\bar{V}_k^\circ$	molar volume components i, k, cm³/mol
x	mole fraction

x_{AO}	mole fraction of component A at interface
x_{AL}	mole fraction of component A at end of tube
x_2, x_3	mole fraction of components 2 and 3, in eq 4 and 5
x^i_2	ideal solubility, mole fraction
z, z_k	volume fraction, volume fraction of *k*th component
$\alpha_{solvent}$	hydrogen bonding factor, dimensionless ($=x/x^i_2$)
η, η_M, η_2	viscosity, cP
μ_B	viscosity of component B, cP
ξ_A	geometric parameter component A, dimensionless
ρ	average total mass concentration, g/cm^3
ρ_A	mass concentration component A, g/cm^3
σ	collision diameter, Å
ω_{AO}	mass fraction component A at interface
ω_{AL}	mass fraction component A at end of tube

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Standard Enthalpy of Formation of Tetrapotassium Pyrophosphate

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The standard enthalpy of formation of tetrapotassium pyrophosphate is −773.3 kcal mol^{-1}; it was determined from the enthalpies of solution of K_2HPO_4, H_2O, and $K_4P_2O_7$ in 10 *m* HCl at 40 °C and from the heat capacities of these compounds and the standard enthalpies of formation of K_2HPO_4 and H_2O.

Introduction

The enthalpy of formation of tetrapotassium pyrophosphate is an important quantity in the development of processes for the manufacture of potassium phosphate fertilizers. It was determined from the enthalpies of formation of K_2HPO_4 and H_2O and the enthalpy of the reaction

$$2K_2HPO_4 = K_4P_2O_7 + H_2O \qquad (1)$$

at 25 °C.

Materials. Reagent-grade dipotassium orthophosphate, K_2HPO_4 (gram formula weight = 174.1834), was recrystallized from distilled water and dried by vacuum desiccation over $MgClO_4$. Chemical analysis showed it to contain 40.7% P_2O_5 and 54.1% K_2O (stoichiometry: 40.75% P_2O_5 and 54.08% K_2O).

Tetrapotassium pyrophosphate, $K_4P_2O_7$ (gram formula weight = 330.3514), was prepared by heating reagent-grade dipotassium orthophosphate in a platinum dish at 600 °C for 21 h and allowing the product to cool to room temperature in a desiccator over $MgClO_4$. Chemical analysis showed the material to contain 57.1% K_2O and 42.98% P_2O_5 (stoichiometry: 57.03% K_2O and 42.97% P_2O_5). None of the P_2O_5 was in the ortho form. The calorimetric solvent was prepared by diluting reagent-grade hydrochloric acid with water to 9.93 *m* HCl as determined by alkalimetric titration.

Calorimeter. The solution calorimeter, the method of measurement, and the corrections applied have been described (*1*, *3*). The defined thermochemical calorie (1 cal = 4.1840 absolute J) was used to convert electrical energy to thermal energy.

Procedure. In a preliminary run in which samples of the solution taken at 10-min intervals were analyzed for total and orthophosphate P_2O_5, the results showed that 8.5 g of $K_4P_2O_7$ was completely hydrolyzed in 30 min at 40 °C in 850 mL of 10 *m* HCl.

The enthalpy of reaction of eq 1 at 40 °C was determined by the scheme

$$\text{ampule } K_2HPO_4 + \text{solvent} = \text{solution A} \qquad (2)$$

$$\text{ampule } H_2O + \text{solvent} = \text{solution B} \qquad (3)$$

$$\text{ampule } K_4P_2O_7 + \text{solution B} = \text{solution A} \qquad (4)$$

and

$$\Delta H_1 = 2(\Delta H_2) - \Delta H_3 - \Delta H_4 \qquad (5)$$

where ΔH_1 is the enthalpy of reaction 1 in calories and ΔH_2, ΔH_3, and ΔH_4 are the enthalpies of reactions 2, 3, and 4, respectively, in cal/mol of the materials in the ampules.

Temperature changes during dissolution were arbitrarily limited to 1 °C, which determined the sample size of tetrapotassium pyrophosphate and thus, by stoichiometry, the sample size of dipotassium orthophosphate. The stoichiometric amount of water