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Diffusivity and Solubility of 1,3-Butadiene in Heptane and Other Properties of Heptane–Styrene and Aqueous Potassium Laurate Solutions

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The densities, viscosities, and butadiene solubilities at atmospheric pressure and a temperature of 277 K are reported for various concentrations of aqueous potassium laurate solutions. These measurements were used to indicate the effect of micelle formation and to determine the critical micelle concentration (cmc). The degree of solubilization of butadiene by the aqueous surfactant solution was well represented by an exponential function of the surfactant concentration. The solubility and molecular diffusivity of butadiene are reported for heptane solvent for several temperatures and atmospheric pressure. The solubility of butadiene is also reported for a temperature of 298 K in the complete range of styrene–heptane solutions. In addition, densities and refractive indices are also reported for the styrene–heptane solutions at the same temperature.

Introduction

Butadiene is most frequently commercially copolymerized with styrene at low temperature by using an emulsion polymerization system to produce synthetic rubber. Occasionally the homopolymer, poly(butadiene), is produced also utilizing an emulsion system. In our research we wished to compare the polymerization of butadiene utilizing an emulsion polymerization process with a process using the inert solvent, heptane, in a solution polymerization process. Whereas the actual results for the comparison of polymerization processes will be reported elsewhere, the results of the determination of the solution properties which pertain are reported here.

Solubilities of butadiene were measured by using a constant solvent flow apparatus described previously (*1*). In that paper also may be found solubilities of butadiene in several hydrocarbon solvents for comparison with those reported in this work for heptane solvent. Butadiene solubilities in water were reported by Reed and McKetta (*2*) for temperatures exceeding 310 K which are useful for comparison with that measured at 277 K as reported here. It has been found useful to represent solubility data for highly soluble gases expressing the mole fraction solubility as a logarithmic function of the temperature. Thus, the large range in solubilities that is usually observed can be concisely expressed on one diagram. In addition, as the data frequently indicate, extrapolation can be made to the gas normal boiling point temperature, quite consistently corresponding to a mole fraction of 1, or for the pure liquefied gas. The gas normal boiling point therefore is useful for checking the consistency of the data by extrapolation.

The mole fraction solubility at the prevailing pressure of the solubility experiment can be calculated directly from the relation between the volume of gas dissolved, the volumetric solvent injection rate, pressure, and gas and solvent molar volumes:

$$x_p = [1 + (rV_G)/(PsV_L)]^{-1} \tag{1}$$

Subsequently, considering that Henry's law applies, the solubility at a butadiene partial pressure corresponding to atmospheric pressure can be determined:

$$x = x_p/P_p \tag{2}$$

The gas partial pressure can be calculated from the vapor pressure of the solvent at the particular temperature and assuming that Raoult's law applies to the solvent:

$$P_p = P - P_L(1 - x_p) \tag{3}$$

It can be shown that the Ostwald coefficient is a function of pressure especially for highly soluble gases if it is assumed that Henry's law describes the variation of solubility with partial pressure. This arises because the Ostwald coefficient is essentially a volume ratio. In terms of the Henry's law constant, H, the variation of the Ostwald coefficient with pressure is given by

$$L_p = V_G/[V_L(H - P_p)] \tag{4}$$

It is apparent therefore, that if Henry's law is obeyed the Ostwald coefficient is independent of pressure only if $H \gg P_p$. The Ostwald coefficient corresponding to a gas partial pressure of 1 atm and expressed as a function of the mole fraction solubility is then

$$L = xV_G/V_L(1 - x) \tag{5}$$

Further, there are at least three other ways of defining an Ostwald coefficient as explained recently by Battino (*3*), but the Ostwald coefficient as defined here, which is based on pure gas and pure solvent volumetric properties *before* contact, is considered most explicit and easiest to use. It represents the ratio of the volume of pure gas at a pressure of 101.325 kPa to the volume of deaerated solvent that on contact will form a saturated solution. This definition of Ostwald coefficient is considered most useful because the gas and solvent volumetric properties are most likely to be known accurately, whereas the properties of the solute and solvent components when these comprise the solution are most difficult to define accurately. Similarly, when two-component solvent solutions or "mixed solvents" are utilized as solvents for gases, the solvent composition may be defined on the basis of solute-free compositions, that is, before any gas has actually dissolved in the solvent. Furthermore, there is a measure of the mixed solvent concentration which is rarely used that often best describes densities and refractive indices of mixed solvents. That composition is a *volume* percent or fraction of one component in the solution as calculated on the basis of the pure component properties before they are mixed. It is equivalent to considering, for the purpose of expressing composition only, that there is no volume change on mixing of the solvent components. The advantage of using this composition is that densities and refractive indices will usually be linearly related when expressed as a volume fraction defined in this manner. All other methods of expressing compositions will result in some degree of curvature when describing the relations for solution densities and refractive indices. This phenomenon was previously discussed (*4*).

The increased solubility of organic substances in aqueous surfactant solutions has particular relevance to emulsion polymerization. In emulsion polymerization micellar solutions are

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used to solubilize the monomer and to provide sites for the polymerization. Although a great deal of additional research has followed, the original work of Harkins and co-workers (*5*, *6*) provides a sound basis for elucidating the principles of solubilization and emulsion polymerization. The observation was made that the increment in solubility is not generally proportional to surfactant concentration but is, in fact, greater than that. We report here that the effect of solubilization of butadiene in aqueous potassium laurate is found to be accurately described by an exponential function. It is noted that the surfactant concentrations involved are those above the cmc but below the surfactant solubility limit and the concentration at which the micelles are impeded in their free motion as independently mobile species. There are a number of ways for determining the cmc of aqueous emulsifier solutions. These include the determination of the solution viscosities and calculation of reduced viscosities. Because we had available an accurate densitometer for determining densities of the micellar solutions, we anticipated that the cmc might also be determined by density measurements. The results indicate that no marked change in the density behavior is observed at the cmc, although a change is discernible. Perhaps densities of butadiene-saturated surfactant solutions would have indicated the cmc more dramatically. On the other hand, surprisingly, butadiene solubilities in the surfactant solutions may be used to clearly indicate the cmc. This is subsequently discussed in more detail.

Molecular diffusivities have been measured for dissolving gases at steady state by using a capillary cell technique as previously described (*7*, *8*). The method involves the diffusion of gas through a column of solvent which is confined in a capillary that is connected to an enclosed chamber filled with deaerated solvent. The solvent at the gas–liquid interface is saturated with gas while at the end of the capillary it is solute-free. Thus, a well-defined concentration gradient is available for diffusion. The steady-state absorption rate of the gas is volumetrically determined by observing the rate of disappearance of gas confined in an extension of the capillary tube above the solvent. A tiny bead of saturated solvent is injected into the capillary to entrap a definite volume of gas. Since this bead is saturated with gas, no mass transfer occurs through it; but it serves as a miniature, essentially frictionless, piston confining a measurable volume of gas and permitting readings of the residual gas volumes. It is necessary to meaningfully relate the measured steady-state absorption rate, the barometric pressure, length of diffusion path, and gas solubility to determine the molecular diffusion coefficient. The general diffusion equation written in terms of the mass fluxes of dissolved gas (n_A) and solvent (n_B) may be used to described this relation. In the following differential equation, the first term represents the bulk flow term while the second term represents Fick's law:

$$n_A = (n_A + n_B)\omega_A - \rho D \frac{d\omega_A}{dz} \tag{6}$$

The bulk flow term, or the motion of the column of liquid in the capillary tube, may be evaluated by considering the very small volumetric rate of solute entering the enclosed cell. The upward volumetric displacement of the column of liquid is equal in magnitude to that of the dissolved solute entering the cell but is opposite in sign:

$$n_A/\rho_A = -(n_a + n_B)/\bar{\rho} \tag{7}$$

To evaluate the bulk flow it is necessary to determine the mass concentration of dissolved gas in the dilute solution in the cell, ρ_A, which is related to the effective molal volume of the dissolved gas. Solution of eq 6 utilizing eq 7 results in the following expression for the molecular diffusivity:

$$D_{AB} = n_A L/[\rho_A \ln(1 + \bar{\rho}\omega_{A0}/\rho_A)] \tag{8}$$

With the assumption that the effective density of dissolved butadiene is the same as that of the heptane solvent, a simpler equation for diffusivity is obtained:

$$D_{AB} = n_A L/[\bar{\rho} \ln(1 + \omega_{A0})] \tag{9}$$

The simplest solution for diffusivity is obtained when the bulk flow is completely neglected:

$$D_{AB} = n_A L/\bar{\rho}\omega_{A0} \tag{10}$$

The evaluation of the differential equation (eq 6) for a constant diffisivity requires the assumption that the solution mass concentration along the diffusion path remain constant. For this reason, the flux equation is normally written in terms of the mass (rather than the molar) concentration because it is, in fact, usually more constant in liquid solutions than is the molar concentration. It is of interest also that the diffusivity determined by eq 8–10 corresponds to an average solute concentration along the diffusion path so that it only approximates a diffusivity for infinite dilution.

Experimental Section

The design of apparatus used for measuring the solubilities of butadiene in heptane and in the aqueous potassium laurate solution was essentially the same as that described by Asatani (*1*). Utilized in the apparatus was a constant flow of degassed solvent which was injected at a constant rate into an absorption spiral tube and a buret in which the butadiene was confined over mercury. For the relatively low solubilities of butadiene in water and aqueous surfactant solutions an apparatus having a gas buret of relatively low volume (25 cm^3) was used along with a relatively high solvent injection rate of about 8 cm^3/h. On the other hand, a modified apparatus was used for the solubility determinations for butadiene in the hydrocarbon solvents. A butadiene storage buret of 250 cm^3 was used in conjunction with a solvent infusion rate of about 1 cm^3/h. Since the apparatus was jacketed, constant temperature cooling (or heating) fluid permitted control of the temperature within the apparatus to ±0.1 K. For measurements at 277 K (4 °C) a bath refrigeration unit was used in conjunction with an aqueous ethylene glycol solution to prevent freezing in the circulating bath. Readings of the volume of gas dissolved and volume of deaerated solvent injected were obtained over a time interval of approximately 1 h. The solubility of butadiene was based on a regression line relating gas volume and solvent injection rate. Hence the solubility could be calculated directly for a total pressure corresponding to atmospheric pressure and subsequently corrected to a butadiene partial pressure of 101.325 kPa. At least two replicate measurements were made for each measurement in the pure solvents and aqueous surfactant solutions. On the other hand, it was not possible to exactly reproduce particular styrene–heptane solvent compositions because of preferential vaporization of the heptane during degassing; however, the complete range of composition was investigated. The heptane–styrene solutions were prepared volumetrically, using burets, to the approximate desired concentrations. After degassing, the actual composition was determined by measuring the solution density at 298 K, the latter value being easy to determine with high accuracy. The most concentrated aqueous surfactant solution was prepared by mass; subsequent dilution with distilled water produced the desired concentrations. It was found that the quantity of water actually evaporated during deaeration was sufficiently low so that the effect on the surfactant concentration could be neglected.

The diffusivity of butadiene in heptane was measured at 298 and 323 K by using a steady-state capillary cell method described previously (*7*, *8*). A similar cell was used in this work, a diagram of which is shown in Figure 1. The diffusion cell

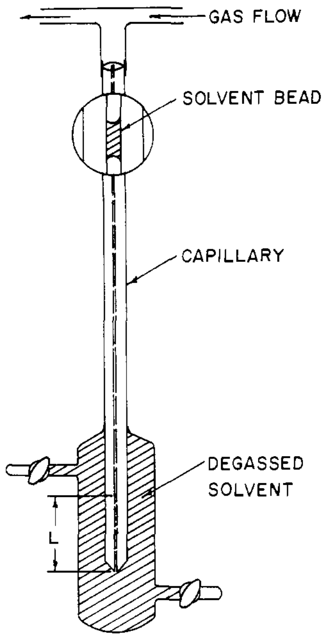

Figure 1. Schematic diagram of capillary tube cell for diffusivity of dissolved gas.

consisted of a precision bore capillary of 1 mm (actually 0.0400 in. i.d.) sealed into a reservoir which could be filled with degassed solvent by means of two miniature high-vacuum stopcocks. The solvent was also allowed to enter approximately 2.5 cm into the end of the capillary tube, the top interface of which was exposed to the gaseous butadiene. It was through this miniature column of solvent located at the end of the capillary that diffusion of butadiene occurred. The top of the capillary tube of the cell was exposed to a very low flow of butadiene saturated with heptane vapor by bubbling through heptane solvent. Thus the gas-liquid interface at top of the solvent column in the capillary was saturated with gas while the bottom, conically ground end, was exposed to deaerated heptane solvent. A period of time (about 20–30 h) calculated to permit a steady-state concentration profile within the solvent in the capillary was allowed to elapse before measurements of absorption rate were made. The rate of diffusion of butadiene through the column of heptane, and of absorption at the interface, was determined by placing a small bead of butadiene-saturated solvent, by means of a syringe, at the top end of the capillary. The bead was a visible device for observing the change in volume of the butadiene trapped in the capillary. The changing position of the bead was accurately measured with a cathetometer. The linear relation between bead position and time permitted the determination of the very low absorption rate with good accuracy using linear regression. The consistent and reliable diffusivity measurements using the capillary cell method was found to depend on a number of factors. These were that the capillary should be of precision bore, completely clean, and no larger in internal diameter than about 1 mm, and that the length of the liquid through which diffusion occurred should be at least 2 cm. Further, temperature control to at least ±0.01 K was required. The small capillary diameter and good temperature control was required to ensure that no convection took place in the column of solvent; the length of the solvent column was so chosen as to eliminate any significant end effects. Small contaminations in the capillary caused sticking of the solvent bead and using unsaturated gas caused evaporation of the bead. Diffisivity measurements are considered possible for all gases or vapors of moderate solubility. Exceptions are those of extremely low solubility such as He or H_2 or those of extremely high solubility such as butadiene at 4 °C. In the former case, the motion of the bead confining the gas is so slow that changes in barometric pressure interfere with the diffusivity measurements. In the latter case, the solute vapor is so soluble (mole fraction greater than 0.70) that the quantity of liquid solution in the capillary continues to increase so that a pseudo-steady-state rate of diffusion through a constant length of liquid cannot realistically be assumed.

Liquid densities were measured by means of an Anton Paar (Austria) Model DMA 60 digital densitometer capable of providing densities of accuracy to at least ±0.0001 provided that the temperature is constant to ±0.01 K. The instrument utilizes a vibrating reed whose frequency is related to the density of the fluid in which it is immersed. The densitometer was calibrated by using the known densities of distilled water, and dried air at the particular barometric pressure. The calibration constant, A, was obtained from the fluid densities and corresponding vibration frequencies, T, according to the following equation:

$$\rho_1 - \rho_2 = (T_1^2 - T_2^2)/A \qquad (11)$$

The instrument requires less than 1 cm^3 of the sample and only a few minutes of time until temperature equilibrium is established. It was expedient, therefore, to introduce at least two solution samples each for increasing concentrations of solution for the density measurements, instead of cleaning the sensing chamber with distilled water, acetone, and dry air after each measurement. Thus, a solution of higher surfactant concentration was introduced, flushed through the sensing chamber, and an approximate density obtained. Then a second sample of the same concentration was flushed through the sensing tube for an accurate density measurement.

Refractive indices of the styrene–heptane mixed-solvent solution were measured by means of a Bausch and Lomb Abbe-3L refractometer. Viscosities of the aqueous potassium laurate solutions were determined by using calibrated Cannon-Fenske viscosity tubes immersed in a constant temperature bath (±0.01 K).

The 1,3-butadiene was purchased from Matheson of Canada having a specified minimum purity of 99.0 mol % and an inhibitor (*tert*-butylcatechol) concentration of 0.01% to prevent polymerization. For these experiments the butadiene was used as received. The volumetric properties of the vapor and liquid were from ref *9*. Reagent grade stryene was purchased from Eastman Kodak and heptane from Matheson Coleman and Bell both having minimum specified purities of 99.0 mol %. The vapor pressures of the solvents were from Reid et al. (*10*). The potassium laurate was purchased from K and K having a specified minimum purity of 95.0%, the best available grade. Fresh aqueous surfactant solutions were frequently prepared and kept stoppered because exposure to the carbon dioxide of the air was stated to cause some formation of the relatively insoluble acid soap. The values of the properties used in the calculations are listed in Table I.

Results and Discussion

The solubilities of butadiene in heptane are listed in Table I as the mole fraction and Ostwald coefficient for a butadiene partial pressure of 101.325 kPa and temperatures of 277, 298, and 323 K. The solubility data are compared with those of butadiene in other solvents (1) including water (2) in Figure 2. It is apparent from Figure 2 that butadiene is extremely soluble in heptane, more soluble than in ethyl acetate for example, another essentially nonpolar solvent. It is also noted that because the solubility of butadiene is only some 2% higher in styrene than it is in heptane at 277 K, it is assumed that the solubility in styrene at other temperatures may also be very similar. The solubility of butadiene in water is shown on another scale because it is some 1000 times less than in heptane. It is noted that there is a marked increase in the solubility in water as the temperature is decreased toward the butadiene normal

Table I. Solubility and Molecular Diffusivity of Butadiene in Heptane Solvent

Solubility

temp, K	mole fracn butadiene	Ostwald coeff L
277.15	0.668	304.6
298.15	0.360	91.0
323.15	0.210	45.3

Diffusivity

		10^5 × diffusivity, cm²/s		
temp, K	av butadiene concn, mass fracn	exptl	Tyn–Calus (eq 14)	Hayduk–Minhas (eq 15)
298.15	0.111	3.51	3.70	3.58
			(5.4)[a]	(2.0)[a]
323.15	0.052	4.66	5.08	4.95
			(9.0)[a]	(6.2)[a]

Parachor, Viscosity, and Molar Volume at the Normal Boiling Point

	molar vol V, cm³/mol	parachor P	viscosity, mPa·s 298.15 K	viscosity, mPa·s 323.15 K
heptane	164.0	311.3	0.3967	0.3128
butadiene	81.6	168.0		

Molar Volume[b] of Butadiene Vapor and Solvents

	temp, K 277.15	298.15	323.15
V_G (butadiene)	21698	23791	25807
V_L (heptane)	143.4	147.0	151.5
V_L (styrene)	113.8		

[a] % deviation. [b] In cm³/mol.

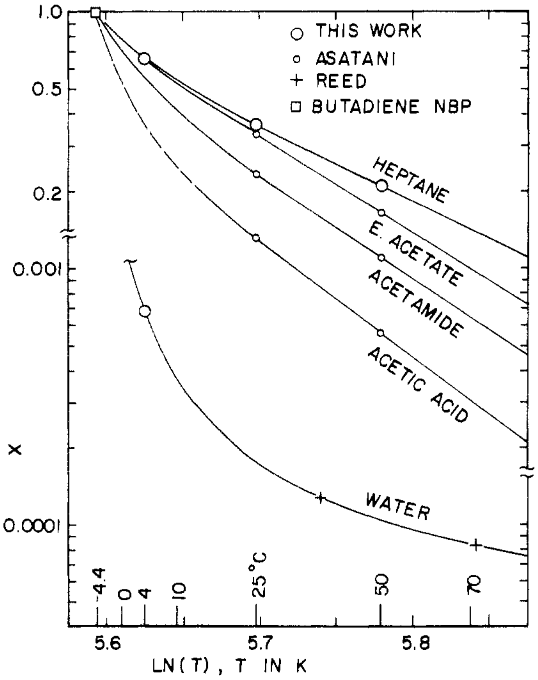

Figure 2. Solubilities of 1,3-butadiene in water, heptane, and other solvents at a butadiene partial pressure of 101.325 kPa.

Table II. Solubility of 1,3-Butadiene in Styrene–Heptane Mixed Solvent Solutions for a Partial Pressure of 101.325 kPa and a Temperature of 277.15 K

solvent composition[a] mole fracn styrene	solvent composition[a] vol fracn styrene	butadiene solubility mole fracn x	butadiene solubility Ostwald coeff L
0.000	0.000	0.668	304.5
0.100	0.078	0.682	324.7
0.144	0.115	0.688	344.0
0.259	0.220	0.698	369.6
0.315	0.269	0.703	383.2
0.486	0.430	0.704	400.1
0.751	0.705	0.698	413.9
0.879	0.853	0.692	415.3
0.968	0.960	0.683	407.4
1.000	1.000	0.683	410.8

[a] On a solute-free basis.

Table III. Density and Refractive Index for Styrene–Heptane Mixtures at 298.15 K

styrene concn mole fracn	styrene concn vol fracn	density, g/cm³	$n^{25}{}_D{}^a$
0.00	0.00	0.6789	1.386
0.00	0.00	0.6795[b]	
0.123	0.100	0.7011	1.403
0.240	0.200	0.7234	1.421
0.351	0.300	0.7458	1.434
0.457	0.400	0.7684	1.450
0.558	0.500	0.7906	1.465
0.654	0.600	0.8132	1.483
0.746	0.700	0.8351	1.498
0.834	0.800	0.8575	1.514
0.919	0.900	0.8794	1.529
1.00	1.00	0.9012	1.544
1.00	1.00	0.9013[c]	

[a] Refractive index. [b] Reference *15*. [c] Extrapolated from data of ref *9*.

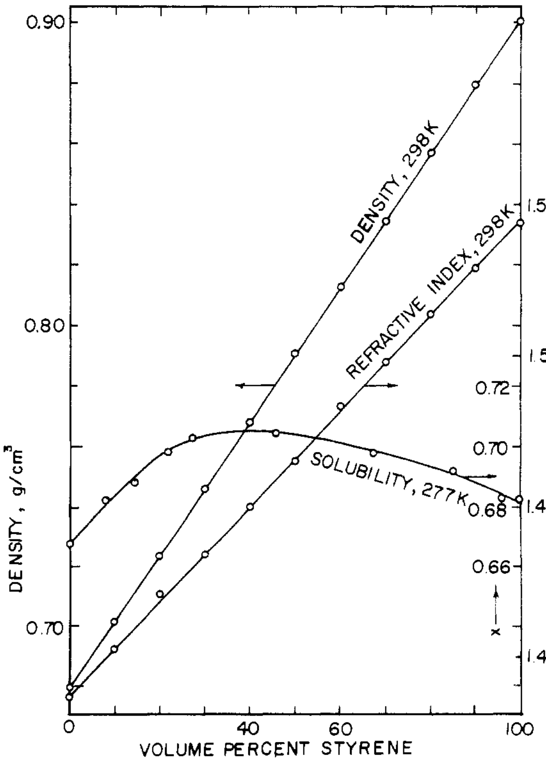

Figure 3. Density and refractive index of styrene–heptane solutions at 298.15 K (25 °C) and butadiene solubility at 277.15 K (4 °C).

boiling point. It is considered that a graphical representation of this type is most useful to test the consistency of solubility data.

The solubilities of butadiene in styrene–heptane mixed solvent solutions at 277 K are also listed in Table II, whereas the densities and refractive indices of the styrene–heptane solutions for a temperature of 298 K are listed in Table III. These data are shown in Figure 3 and plotted as a function of the *volume* percent of styrene. Within experimental error, both the density and refractive index form completely linear relations when the solvent composition is expressed in this way. The scale for the solubilities of butadiene in the mixed solvent solution has been

Table IV. Density, Viscosity, and Butadiene Solutibility in Aqueous Potassium Laurate Solutions at 277.15 K (4 °C)

surfactant concn, g/dm³	density, g/cm³	viscosity, mPa·s (cP)	reduced viscosity, dm³/g	solubility: mole fracn	solubility: Ostwald coeff
0.0	1.0000	0.015 47		0.000 68	0.806
0.528	1.0001	0.015 51	0.004 96		
0.970	1.0002	0.015 53	0.004 11		
1.51	1.0003	0.015 69	0.009 22		
2.00	1.0003	0.015 72	0.007 99		
2.55	1.0004	0.015 98	0.012 85		
3.96	1.0006	0.016 05	0.009 37		
5.17	1.0007	0.016 20	0.009 17	0.000 72	0.852
5.96	1.0009	0.016 21	0.008 04		
9.92	1.0013	0.016 49	0.006 63		
10.05				0.000 80	0.949
15.06	1.0018	0.016 72	0.005 36	0.000 93	1.112
19.95	1.0024	0.017 37	0.006 15	0.001 05	1.252
25.18				0.001 20	1.434
26.84	1.0031	0.017 92	0.005 89		
30.49	1.0035	0.018 55	0.006 53	0.001 43	1.672
35.31				0.001 60	1.897
40.11				0.001 85	2.220

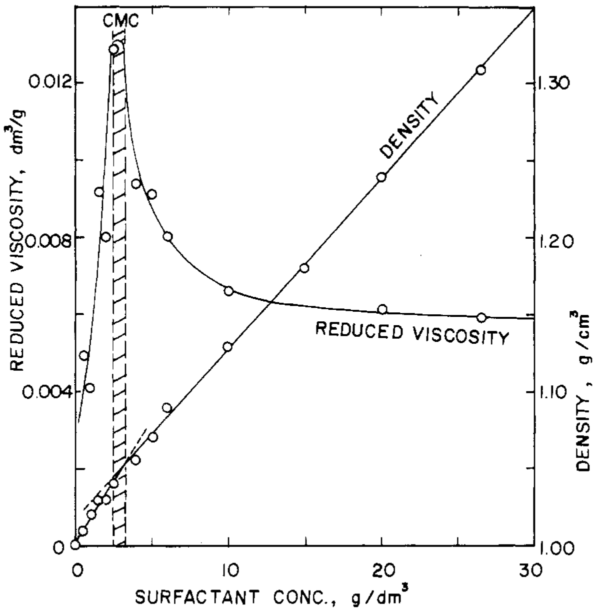

Figure 4. Density and reduced viscosity of aqueous potassium laurate at 277.15 K (4 °C).

expanded because, in fact, the solubility is nearly constant, varying less than 4% from the minimum solubility in heptane to a maximum solubility at a solvent concentration of some 40 vol % styrene. The data for the densities of pure styrene and heptane at 298 K are favorably compared with those previously published as shown in Table III.

In Table IV are listed the density, viscosity, and butadiene solubility data for aqueous potassium laurate solutions for a temperature of 277 K. The densities and calculated reduced viscosities are shown as a function of the surfactant concentration in Figure 4. The density data indicate a different slope in the region of surfactant concentration in which butadiene solubilization takes places when compared with the density–concentration relation below the cmc. However, to be able to observe this difference in slope, which is relatively small, one requires very accurate density data. The more conventional indication of the cmc is clearly represented by the relation between the reduced viscosity and the surfactant concentration. It is possible to give only a cmc range, 2.5–3.3 kg/m³ (g/dm³). When the butadiene solubility at 277 K is plotted as a function of surfactant concentration on a semilog plot as shown in Figure 5, again a clear indication of the effect of butadiene solubilization is observed. This suggests that as the surfactant concentration increases not only is the solubility increased because the number of micelles increases but also the micelles already containing solute expand and imbibe yet additional solute. The exponential function which best describes this relation has the following form:

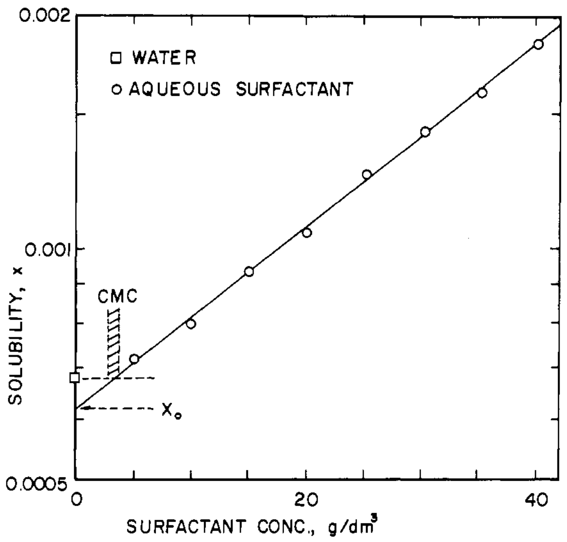

Figure 5. Semilog diagram for solubility of butadiene in aqueous potassium laurate solutions at 277.15 K.

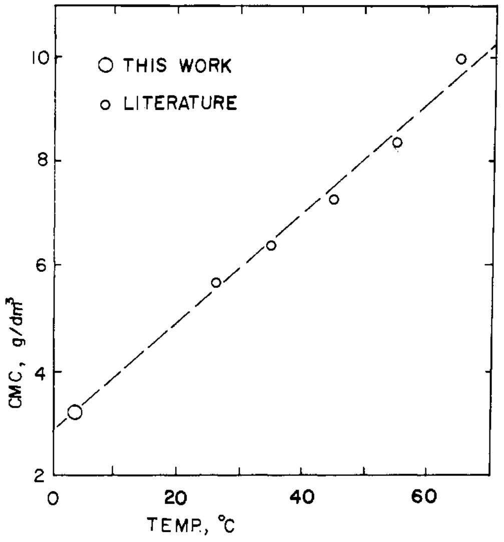

Figure 6. The critical micelle concentration (cmc) as a function of temperature for aqueous potassium laurate solutions.

$$x = x_0 e^{bC} \tag{12}$$

The actual constants for this particular relation are

$$x = 6.20 \times 10^{-4} e^{0.0272C} \tag{13}$$

An estimate of the cmc may be made by assuming that the solubility of butadiene in surfactant concentrations below the cmc is the same as that in water. Then the intersection of the two lines as shown in Figure 5 yields the cmc which is, in this case, 3.40 kg/m³. Because of the uncertainties involved, again it is more realistic to give a range for the cmc of from 3.0 to 3.8 kg/m³ which compares favorably with the previous estimates of the cmc. In Figure 6 the cmc for aqueous potassium laurate is shown as a function of temperature by using the data of Stearns et al. (*6*) and of Klevens (*11*). As we might expect, the cmc of the solid surfactant diminishes as the temperature is reduced. We have no basis for assuming a linear relation between the temperature and the cmc, however; hence the line in Figure 6 is indicated as a dashed line.

The average molecular diffusivities of dissolved butadiene in heptane at atmospheric pressure and temperatures of 298 and 323 K as obtained in this work are listed in Table I. For comparison with these data we wished to predict the molecular diffusivities at infinite dilution for this system using the correlation of Tyn and Calus (*12*) and Hayduk and Minhas (*13*). The correlation equations expressed in terms of the molar volumes at the normal boiling point (V_A, V_B) as well as the parachors (P_A, P_B) and solvent viscosity are given in the order mentioned:

$$D_{AB}{}^0 = 8.93 \times 10^{-8} T V_A{}^{1/6} (P_B/P_A)^{0.6}/(\mu_B V_B{}^{1/3}) \quad (14)$$

$$D_{AB}{}^0 = 1.55 \times 10^{-8} T^{1.29} P_B{}^{0.5}/(\mu_B{}^{0.92} V_B{}^{0.23} P_A{}^{0.42}) \quad (15)$$

Both of the above equations are expected to yield good estimates of molecular diffusivities for nonpolar, nonassociating solutions. It is noted that for the evaluations using the above equations, values of the parachor as well as molar volume at the normal points are required for both solute and solvent. Whereas the other necessary properties are readily available, the parachor for butadiene is not. Nor is the estimation method for the parachor as outlined by Quayle (*14*) explicit for the particular combination of carbon bonds as found in 1,3-butadiene. Hence, there is no value for the parachor of butadiene in the list by Quayle of some 1600 compounds. Gallant (*15*), however, gives a value for the surface tension for (saturated) liquid butadiene which can be used to estimate the parachor as suggested by Sugden (*16*):

$$P = \sigma^{0.25} M/\rho_L \quad (16)$$

Based on this equation the parachor for butadiene is estimated to be P_A = 168.0. The estimates of diffusivity of butadiene in heptane as obtained by using eq 14 and eq 15 conform unusually well to the experimentally determined diffusivities. It is noted that the Hayduk–Minhas correlation is based on much of the same original data and is slightly more complex than the correlation of Tyn and Calus.

Conclusions

The solubilities of the highly soluble monomer, 1,3-butadiene, are reported for atmospheric pressure and several temperatures in heptane solvent, and for 277.15 K (4 °C) in the mixed solvent solutions of heptane and styrene, and aqueous potassium laurate. For the heptane–styrene solutions, the densities and refractive indices are reported for 298.15 K. For the same temperature, the densities and viscosities are reported for aqueous potassium laurate solutions. The molecular diffusivities of 1,3-butadiene dissolved in heptane are also reported for two temperatures.

The above results are considered useful in interpreting polymerization experiments involving solution and emulsion polymerization of 1,3-butadiene. They should also prove useful in developing theories of solubility and molecular diffusivity. The accurate analysis of density appears to be a good method for obtaining the solution composition of mixed solvent solutions.

Glossary

A	constant in eq 11 relating density and vibrating frequency
b	constant in exponential equation for effect of surfactant
C	surfactant concentration, g/dm^3, kg/m^3
D	diffusion coefficient in liquid solution, cm^2/s
$D_{AB}{}^0$	diffusivity of A in B at infinite dilution of A, cm^2/s
H	Henry's constant, mole fraction/atm
L	Ostwald coefficient corresponding to a gas partial pressure of 1 atm
L	diffusion path length, cm
M	molar mass, g/mol
n	mass flux, g/(cm^2 s)
n_D	refractive index
P_p	gas partial pressure, atm
P	total pressure, atm
P	parachor
P_L	vapor pressure of liquid, atm
s	gas absorption rate, cm^3/s
t	temperature, °C
T	temperature, K
T	frequency of vibration of densitometer reed, cycle/s
r	solvent infusion rate, cm^3/s
V_G	molar volume of gas at a partial pressure of 1 atm, cm^3/mol
V_L	molar volume of solvent, cm^3/mol
V	molar volume at the normal boiling point temperature, cm^3/mol
x	mole fraction dissolved gas in solution corresponding to a gas partial pressure of 1 atm
x_p	mole fraction dissolved gas in solution corresponding to a gas partial pressure of p atm
x_0	reference solubility, mole fraction
z	position along diffusion path, cm

Greek Letters

μ	solvent viscosity, mPa·s (cP)
ρ	solvent density, g/cm^3
ρ	total mass concentration, g/cm^3
$\bar{\rho}$	average mass concentration, g/cm^3
σ	surface tension, mN/m (dyn/cm)
ω	mass fraction of a component in liquid solution

Subscripts

A, G	solute (gas) component
B, L	solvent (liquid) component
p	at varying solute partial pressure

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