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Cluster Diffusion in Liquids

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Diffusion in concentrated, non-ideal liquid solutions may take place not only through motion of single molecules but also through movement of groups of molecules, or "clusters." Analyzing this cluster diffusion leads to predictions that the diffusion coefficient can vary with the square root of the usual activity corrections to diffusion. These predictions seem consistent with experiments, particularly in highly non-ideal solutions.

SCOPE

The purpose of this article is to describe diffusion in concentrated liquid solutions. Such solutions are frequently highly non-ideal. The diffusion coefficient D in liquids is often estimated from the equation

$$D = D_0 \left(\frac{\partial \ln a_1}{\partial \ln x_1} \right)$$

The reference value D_0 in this equation can be estimated from correlations like the Stokes-Einstein equation, which is exact for a single spherical solute molecule moving in a viscous continuum. The thermodynamic factor in parentheses, which can be rationalized with irreversible thermodynamics (de Groot and Mazur 1962), is known to be accurate in highly dilute salt solutions. However, in highly non-ideal solutions, this equation can be inaccurate. Some of the inaccuracy doubtless results from the limits of models like a single solute sphere in a continuum, a picture which is less valid in concentrated solutions of similar size (e.g., Cullinan and Cusik 1967, Dullian 1972, Ghai et al 1973). More of the inaccuracy may come from an incorrect thermodynamic correction.

The approach here is to consider diffusion not only of single solute molecules, but also of small clusters of solute molecules. For this case, the diffusion coefficient becomes

$$D = \frac{kT}{2\pi\eta\xi}$$

where the correlation length ξ is approximately the average size of a cluster. This approach retains the same temperature and viscosity dependence as the Stokes-Einstein equation. The factor 2π in place of 6π is not a major change. However, both the diffusion coefficient D and the length ξ vary dramatically with the thermodynamic factor.

The analysis of cluster diffusion is based largely on theories of diffusion near the critical solution temperature or consolute point (Swift 1968). In this region, both the size and the lifetime of concentration fluctuations become large, and the diffusion coefficient drops sharply to approach zero. Theories developed to explain this behavior have not been used to predict concentration dependent diffusion farther from the consolute point. Here, we make and test such predictions.

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CONCLUSIONS AND SIGNIFICANCE

In concentrated non-ideal solutions, the diffusion coefficient is shown to be

$$D = D_0\left[\frac{1}{1+\frac{K}{x_1x_2}\left(\frac{\partial \ln x_1}{\partial \ln a_1}-1\right)}\right]^{1/2}$$

where K is a constant of order one half. This prediction retains the reference value D_0, and so implies similar temperature, viscosity, and solute size dependence as earlier predictions. However, the exponent (½) on the quantity in brackets indicates a radically different dependence on the thermodynamic correction factor. This different dependence is a consequence of cluster diffusion.

The variation of diffusion coefficient with the square root of the thermodynamic correction factor is observed for highly non-ideal systems where earlier predictions failed (Vignes 1968). Moreover, the predicted variation supports that observed empirically in other non-ideal solutions (Kasanovich and Cullinan 1976). The predictions are also consistent with the temperature dependence of diffusion near the consolute point.

The results presented here allow improved estimates of diffusion in concentrated liquid solutions. The idea of cluster diffusion has provided further insight about liquid solution behavior.

The description of diffusion in concentrated liquid solutions depends on the assumption that clusters of solute molecules can diffuse as a unit through a liquid solution. Such clusters are similar to the concentration fluctuations which occur near the critical solution temperatures or consolute points. Such points are shown schematically as the x's in the insert to Figure 1. They represent that temperature and composition where two liquids become miscible in all proportions. Where this occurs with increasing temperature, an upper consolute point is observed. Where it requires a decrease in temperature, a lower consolute point is found.

Near this point, the binary diffusion coefficient drops precipitously to zero, as shown in Figure 1. This drop, which occurs at both upper and lower consolute points, has been explained in three different ways, reviewed briefly here.

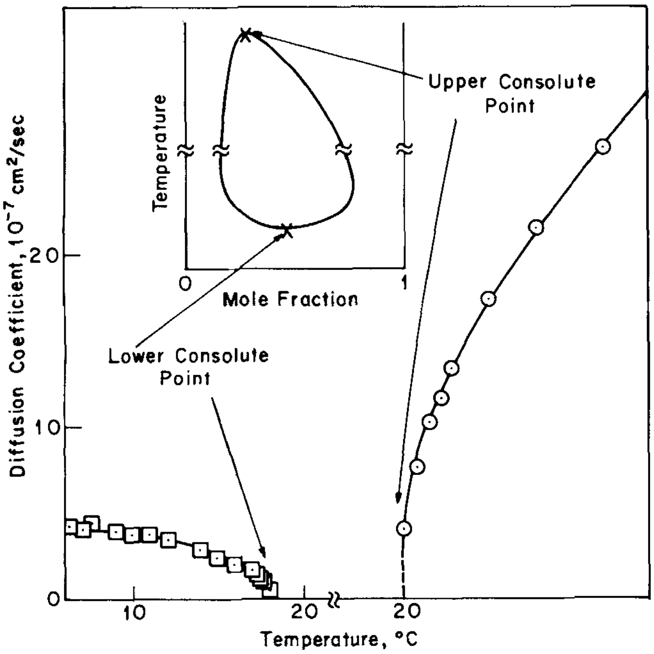

Figure 1. Diffusion near consolute points: Diffusion drops precipitously at these points, which are schematically illustrated in the insert. The data are for nitrobenzene-hexane (○, Claersson and Sundelöf 1957) and for triethylamine water (□, Haase and Siry 1968).

The first explanation for the variation in Figure 1 rests on the modification of relations like the Stokes-Einstein equation (Turner 1975a,b)

$$\begin{aligned} D &= D_0\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right) \\ &= \frac{kT}{6\pi\eta r_0}\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right) \\ &= \frac{1}{6\pi\eta r_0}\left(x_1\frac{\partial \mu_1}{\partial x_1}\right) \end{aligned} \tag{1}$$

At the consolute point, $(\partial \ln a_1/\partial \ln x_1)$ equals zero, but D_0 or $[kT/6\pi\eta r_0]$ is finite. Thus Equation (1) correctly predicts that diffusion at the consolute point is zero.

However, Equation (1) does not correctly predict all aspects of diffusion near the consolute point. To illustrate this, consider the system hexane-nitrobenzene (Figure 1). This solution is very nearly regular, i.e.,

$$\mu_1 = \mu_1{}^0 + kT \ln x_1 + \omega x_2{}^2 \tag{2}$$

At the consolute point of such a solution, one may show that $x_1 = x_2 = 0.5$, and that $\omega = 2kT_C$, where T_C is the consolute temperature (Prigogine and Defay 1954). As a result, one finds that at the critical composition

$$\frac{\partial \ln a_1}{\partial \ln x_1} = 1 - 4x_1x_2T_C/T = 1 - \frac{T_C}{T} \tag{3}$$

Combining with Equation (1)

$$D = D_0\left[\frac{T-T_C}{T}\right] \tag{4}$$

The linear temperature variation in brackets is much greater than the temperature variation of D_0 near the consolute point. However, this linear variation is not observed in Figure 1, so that Equation (1) and Equation (4) are inconsistent with experiment.

This failure of Equation (1), a fixture of many lectures, may be initially difficult to accept. To try to save this equation, it might be argued that the regular solution model is wrong, that D_0 undergoes some unusual variation with temperature, or that some major effect like reference velocity or viscosity has been omitted. None of these arguments are supported by experiment. The regular solution model is inexact near the critical point, but not dramatically so

(Stanley 1971). Indeed, the system hexane-nitrobenzene was chosen for study because it does closely fit this model (Haase and Siiry 1968). Any bizarre temperature variation of D_0 should also appear in the self-diffusion coefficient, but it does not (Leister 1970, Harman et al 1972). Factors like viscosity do show anomalous behavior at consolute points (Mujake et al 1977) but the effects are small, of the order of 20%, for viscosity. This is much smaller than the drop in diffusion of at least 100,000.

Equation (1) might also be salvaged by arguing that it can be rigorously derived from non-equilibrium thermodynamics, and hence is equivalent to the concept of entropy production. Equation (1) can be so derived. However, the derivation includes the assumption that the diffusion flux varies linearly with the appropriate thermodynamic force, in this case the gradient of chemical potential (de Groot and Mazur 1962, Fitts 1962, Katchalsky and Curran 1967). It is this assumption of linearity which is currently being questioned, not only for diffusion but for viscosity, thermal conductivity, and magnetization. It is being questioned because it is not supported by experiment (Stanley 1971).

The second explanation of the results in Figure 1 assumes that Fick's law fails in this region (Anisimov and Perelman 1966). This failure means that

$$D = D_0 \left[1 + Z \nabla^2 x_1 + \ldots\right] \tag{5}$$

where Z is a constant. In other words, the linear form of Fick's law must now include higher terms, just as the flow of non-Newtonian fluids can require higher terms than that in Newton's law of viscosity. While the details can not be concisely given, this approach also predicts that the diffusion should approach zero at a consolute point and can predict the correct temperature dependence.

However, Equation (5) does not predict the concentration profiles in a free diffusion experiment. In such an experiment, an initially sharp concentration profile is formed, and that profile decays with time. If Fick's law is correct, the concentration gradient in such an experiment should vary with the square root of time; if Equation (5) is correct, the variation should be with the fourth root of time. Experiments near the consolute point show variation with the square root of time (Brunel and Breuer 1971). Thus Equation (5) is not valid over the current experimental range.

The third explanation of the data in Figure 1 is that extended in this article. It is assumed that long range fluctuations dominate behavior near the consolute point. When fluctuations of concentration and of fluid velocity couple, diffusion occurs. The concentration fluctuations include both single solute molecules and clusters of molecules. The velocity fluctuations exist even when the average fluid velocity is zero. The result is like turbulent "eddy diffusion," but one in which there is no flow.

DIFFUSION VS. CORRELATION LENGTH

Cluster diffusion is most easily described in terms of time-integrated velocity correlation functions (Reed and Gubbins 1973) which for dilute solutions may be written as

$$D = \int_0^\infty \langle v_1(0)\, v_1(t) \rangle \, dt \tag{6}$$

However, in a concentrated solution, the local concentration as well as the velocity may undergo significant fluctuations. If these fluctuations couple, then the physical properties of the solution will be altered (Debye 1959, Fixman 1962). In this case, the diffusion coefficient will become (Ferrell 1972)

$$D = \frac{\langle G(r)\, F(r) \rangle}{\langle G(r) \rangle} \tag{7}$$

where $F(r)$ is the time-integrated velocity correlation function and $G(r)$ is the concentration correlation function

$$G(r) = \langle C_1(r)\, C_1(r') \rangle \tag{8}$$

In other words, the diffusion coefficient is equal to the time-integrated velocity correlation function averaged over fluctuations in concentration. Equation (7) implies a major assumption, that fluctuations in concentration and in velocity are statistically independent. This implies that the frequent, shorter range variations in solution properties contribute more effectively to diffusion than infrequent long-range fluctuations (Swift 1968, Kawasaki 1970).

The next step is estimating values of $F(r)$ and $G(r)$. For the former, we assume the spherically symmetric form (Ferrell 1970)

$$F(r) = \frac{kT}{2\pi\eta r} \tag{9}$$

This implies that increases in temperature increase velocity fluctuations. More importantly, it implies that the viscosity can still be defined on a microscopic level. In a sense, Equation (9) is similar to that used in the Stokes-Einstein equation, where the surroundings are treated as a viscous continuum.

The concentration correlation function $G(r)$ has different forms for highly dilute and for concentrated solutions. For highly dilute solutions, it is a large constant at less than the molecular radius and zero at larger radii. When this result is combined with Equations (7) and (9), the result is the Stokes-Einstein equation, thus justifying Equation (9) (Ferrell 1970).

For concentrated solutions, we return to the classical theory of the critical point and adopt the Ornstein-Zernike form (Stanley 1971)

$$G(r) = \frac{a}{r} e^{-r/\xi} \tag{10}$$

where a is a length on the order of molecular size; and ξ is the correlation length characteristic of the size of the concentration fluctuations, a rough measure of the average size of any diffusing clusters. The diffusion coefficient is found by combining Equations (7), (9), and (10)

$$D = \frac{4\pi \int_0^\infty \left(\frac{a}{r} e^{-r/\xi}\right)\left(\frac{kT}{2\pi\eta r}\right) r^2 \, dr}{4\pi \int_0^\infty \frac{a}{r} e^{-r/\xi} r^2 \, dr} = \frac{kT}{2\pi\eta\xi} \tag{11}$$

In other words, in concentrated solutions, it is the size of diffusing clusters rather than of diffusing solutes which controls diffusion.

CORRELATION LENGTH VS. CHEMICAL POTENTIAL

Of course, Equation (11) is useful only if one can estimate the quantity ξ, and in particular, its relation to the chemical potential and activity coefficients. Such an estimation will predict how the diffusion coefficient should vary with concentration.

Near the consolute point, common expressions for the chemical potential fail and must be replaced by more elaborate theories. At least three generations of these theories are extensively described in the literature (e.g., Stanley 1971), so only the most important results are quoted here. These results are most easily expressed in terms of the deviations of the temperature and composition from the consolute point. Specifically, they are that

$$\xi^2 \propto \left(\frac{T}{T_C} - 1\right)^{-2\nu} \quad \text{when} \quad x_1 = x_{1C}$$
$$\propto (x_1 - x_{1C})^{1-\delta} \quad \text{when} \quad T = T_C \tag{12}$$

where the subscript C indicates the consolute values, and ν and δ are the exponents calculated theoretically.

While no exact theory for these exponents exists, there are accurate approximations. Classical approaches based, for example, on the van der Waals equation, predict that $\nu = 1/2$ and that $\delta = 3$. More exact formulations (based largely on the Ising model) predict a similar value for ν of about 0.62. However, they predict that $\delta = 5$, significantly different than the classical results. We will use the Ising results in the discussion that follows.

Farther from the consolute point, the common models of the chemical potential are more accurate. The relationship between this potential and the correlation length ξ can be found from the equations of Kirkwood and Buff (1951)

$$\frac{1}{kT}\frac{\partial \mu_1}{\partial x_1} = \frac{1}{x_1} - \frac{n x_2 (g_{11} + g_{22} - 2\, g_{12})}{1 + n x_1 x_2 (g_{11} + g_{22} - 2\, g_{12})} \tag{13}$$

where n is the number of molecules per volume and where

$$g_{ij} = \int_0^\infty G_{ij}\, dr$$
$$= \int_0^\infty \frac{a_{ij}}{r} r^{-r/\xi_{ij}}\, 4\pi r^2\, dr$$
$$= 4\pi\, a_{ij}\, \xi_{ij}^2 \tag{14}$$

To simplify the analysis, we assume that

$$4\pi a \xi^2 = 4\pi a_{11}\xi_{11}^2 + 4\pi a_{22}\xi_{22}^2 - 8\pi a_{12}\xi_{12}^2 \tag{15}$$

Combining Equations (13-15), and rearranging,

$$\xi = \left\{ \left(\frac{1}{4\pi a n}\right) \frac{1}{x_1 x_2} \left[\frac{kT}{x_1} \frac{\partial x_1}{\partial \mu_1} - 1 \right] \right\}^{1/2} \tag{16}$$

The correlation length depends on the square root of the chemical potential.

Equation (16) has one obvious and major failing: It predicts that for an ideal solution, the correlation length is zero. This is nonsense, because the correlation length can not become smaller than the average diameter of the molecules. As a result, we empirically modify Equation (10)

$$\xi = 2 r_0 \left\{ 1 + \frac{1}{16\pi r_0^2 a n} \frac{1}{x_1 x_2} \left[\frac{kT}{x_1} \frac{\partial x_1}{\partial \mu_1} - 1 \right] \right\}^{1/2} \tag{17}$$

The quantity r_0 is characteristic of the molecular radius. This modification does not affect the results near the consolute point but it does insure that Equation (17) reduces to the Stokes-Einstein equation for dilute solutions.

A COMPARISON OF PREDICTIONS

The differences between the approaches suggested by Equation (1) and Equation (5) and those developed above are made clearer by considering a special case, the van Laar solution. For this case, the chemical potential is (King 1969)

$$\mu_1 = \mu_1^0 + kT \ln x_1 + \frac{A}{\left(1 + \frac{A x_1}{B x_2}\right)^2} \tag{18}$$

where A and B are adjustable parameters. Since at the consolute point $\partial \mu_1/\partial x_1 = \partial^2 \mu_1/\partial x_1^2 = 0$,

$$A = \frac{27 x_{2C} k T_C}{2(1 + x_{1C})(1 + x_{2C})^2} \tag{19}$$

where the subscript C again indicates the critical composition and temperature. The parameter B can be found by rotating the indices.

These expressions can now be combined with Equation (1)

$$D = D_0 \left\{ \frac{x_1}{kT} \frac{\partial \mu_1}{\partial x_1} \right\}$$
$$= D_0 \left\{ \frac{27 T_C x_{1C}^2 x_{2C}^2 x_1 x_2}{T((1 + x_{1C}) x_{2C} x_1 + (1 + x_{2C}) x_{1C} x_2)^3} \right\} \tag{20}$$

At the consolute composition, this reduces to Equation (4): Diffusion varies linearly with temperature. Other simple thermodynamic models also predict linear dependence. At the consolute temperature, there is no simple concentration dependence except for a regular solution, when diffusion varies with the square of the deviation of the concentration from the consolute value.

Similar predictions based on the modified form of Fick's law given in Equation (5) are not possible, since this equation is phenomenological. It introduces a new parameter, Z, whose temperature and composition dependence can be adjusted to fit the experimental results. However, one should remember that this theory predicts the wrong time dependence of free diffusion experiments (Brunel and Breuer 1971).

The results from the theory of critical phenomena can be found by combining Equations (11-12)

$$D = D_0 \left(\frac{T}{T_C} - 1\right)^{0.62} \quad \text{when } x_1 = x_{1C}$$
$$= D_0 (x_1 - x_{1C})^{2.0} \quad \text{when } T = T_C \tag{21}$$

where $D_0 (= kT/2\pi\eta r_0)$ is some standard value and the critical exponents are those based on the Ising theory. The value chosen for D_0 or for r_0 is not important here, since the behavior close to consolute point is important.

The results based on cluster diffusion farther from the consolute point can be found by combining Equations (11) and (17)

$$D = D_0 \left[\frac{1}{1 + \frac{K}{x_1 x_2}\left[\frac{kT}{x_1}\frac{\partial x_1}{\partial \mu_1} - 1 \right]} \right]^{1/2} \tag{22}$$

where $D_0 (= kT/4\pi\eta r_0)$ is a reference value and $K (= 1/16\pi r_0^2 a n)$ is a constant characteristic of the system being studied. In highly non-ideal solutions, $\partial \mu_1/\partial x_1$ can approach zero and the term containing K can become large relative to one. In this case, the result for a van Laar solution is

$$D = D_0 \left\{ \frac{T}{27 T_C} \frac{[x_1 x_{2C}(1 + x_{1C}) + x_2 x_{1C}(1 + x_{2C})]^3}{x_{1C}^2 x_{2C}^2} - x_1 x_2 \right\}^{1/2} \tag{23}$$

where $D_0 (= kT/\eta)(an/\pi)^{1/2}$ is again a reference value. At the critical composition, Equation (23) predicts D varies with the square root of temperature. At the critical temperature, no simple composition dependence exists: The variation is linear for a regular solution, and higher for a van Laar solution.

The differences between these results are summarized in Table 1. More physical insight can be found from comparing Equation (22) and Equation (1). Equation (22) is for diffusion of clusters of solute molecules what Equation (1) is for diffusion of a single solute molecule. Both show the same viscosity dependence. Both predict that diffusion varies inversely with solute size. Equation (22) has a constant of $(1/4\pi)$; Equation (1) shows a constant of $(1/6\pi)$, but this value would also be $(1/4\pi)$ if the boundary condition on the rigid sphere was "no stick" instead of "no slip."

The chief difference between Equations (1) and (22) is the dependence on chemical potential or activity coefficient. Equation (1) predicts this dependence is linear, but Equation (22) predicts a more complex dependence involving a square root. As a result, corrections for activity are considerably smaller for cluster diffusion than those expected from Equation (1). Whether this is true will be checked experimentally here.

All the analyses above predict the diffusion coefficient as

$$D = D_0 f\left(\frac{\partial \mu_1}{\partial x_1}\right) \tag{24}$$

The chief difference between approaches is the form of the function f. To compare these different approaches, the three quantities D, $(\partial\mu_1/\partial x_1)$, and D_0 must all be known. The first is found from diffusion measurements, and the second is commonly calculated from vapor pressure determinations. The third must be estimated from earlier theories, which most often calculate an average diffusion coefficient from the values at infinite dilution. These averages vary widely: for example, they can be arithmetic weighted with the mole fraction (Hartley and Crank 1948), arithmetic weighted with the volume fraction (Dullien 1972, Kosanovich and Cullinan 1976), or geometric, weighted with the mole fraction (Vignes 1968). Which average is chosen influences the success of the estimates of diffusion coefficient.

We decided not to choose a single means of estimating D_0, but to use that chosen by each earlier investigator to correlate his or her own diffusion measurements. We did so in the expectation that an investigator chooses the type of average which best supports his or her ideas. This variable choice provides a more stringent test of Equation (22) than of Equation (1), since in almost all cases, the type average is chosen after first assuming Equation (1) is correct.

NEAR THE CONSOLUTE POINT

Results near consolute points are discussed first, followed by results in more ordinary solutions. The first example is the system water-triethylamine, which has a lower critical solution temperature at 18.7C. Diffusion and chemical potential measurements in this system measured by independent groups (Haase and Sirey 1968, Dudley and Tyrell 1973b, Kohler 1951, Counsell 1959) are in good agreement. Dudley and Tyrell suggest that (Darken 1948)

$$D_0 = x_1 D_2^* + x_1 D_2^* \tag{25}$$

where the D_i^*'s are intradiffusion coefficients which have been measured experimentally (Dudley and Tyrell 1973a). Thus Equations (1) and (22) can be critically compared.

The first test of Equation (22), given in Figure 2, shows that the inverse square of the diffusion coefficient is, in fact, proportional to the chemical potential derivative, as predicted by Equation (22). The position of this line gives the magnitude of the parameter K in this equation. Somewhat surprisingly, this value is a strong function of tem-

TABLE 1. PREDICTED CHANGES OF DIFFUSION

Approach	Physical basis	Key equations	Time dependence in free diffusion	Variation with chemical potential	Variation at consolute temperature	Variation at consolute temperature	Remarks
Common activity correction	Empirically modifies results at infinite dilution	Eq. (1) or Eq. (20)	$t^{1/2}$	$D \propto \partial\mu_1/\partial \ln x_1$	$D = D_0\left(1 - \frac{T_C}{T}\right)$	$D = D_0(x_1 - x_{1C})^2$ for a regular solution	Composition dependence lower for a van Laar solution
Modified Fick's law	Includes gradient of La Placian	Eq. (5)	$t^{1/4}$	non-linear	adjustable	adjustable	Phenomenological approach with new adjustable parameters
Critical phenomena theory	Considers effect of concentration fluctuations and failure of chemical potential models	Eq. (21)	$t^{1/2}$	$D \propto \frac{1}{\xi}, \xi = \xi(\mu_1)$	$D = D_0\left(\frac{T}{T_C} - 1\right)^{0.62}$	$D = D_0(x_1 - x_{1C})^2$	Valid only close to consolute point
Cluster diffusion	Considers effect of concentration fluctuations	Eq. (17) or Eq. (23)	$t^{1/2}$	$D = f\left(\sqrt{\partial\mu_1/\partial \ln x_1}\right)$	$D = D_0\left(\frac{T}{T_C} - 1\right)^{1/2}$	$D = D_0(x_1 - x_{1C})$ for a regular solution	Composition dependence higher for a van Laar solution

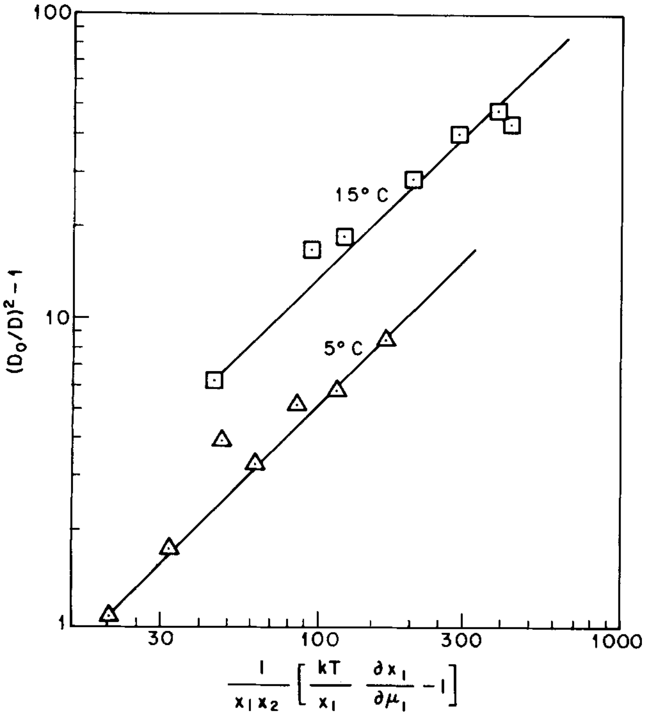

Figure 2. Diffusion of triethylamine in water: The slopes are those predicted from Eq. (22). The values of D (Dudley and Tyrell 1973b) agree closely with those interpolated from Haase and Siry (1968). The values of D_0 and $(\partial\mu_1/\partial x_1)$ are experimental (Dudley and Tyrell 1973a, Counsell 1959).

perature, equal to about 0.05 at 5°C and 0.13 at 15°C. Whether this change is real or a consequence of the large errors involved in calculating $(\partial\mu_1/\partial x_1)$ is uncertain. Using these values, one may estimate the variation of diffusion with concentration which is predicted by Equation (22). As Figure 3 shows, this variation agrees more closely with experiment than that predicted by Equation (1). Unfortunately, it can not be compared with the predictions of Equation (21), because the temperature is lower than the consolute value.

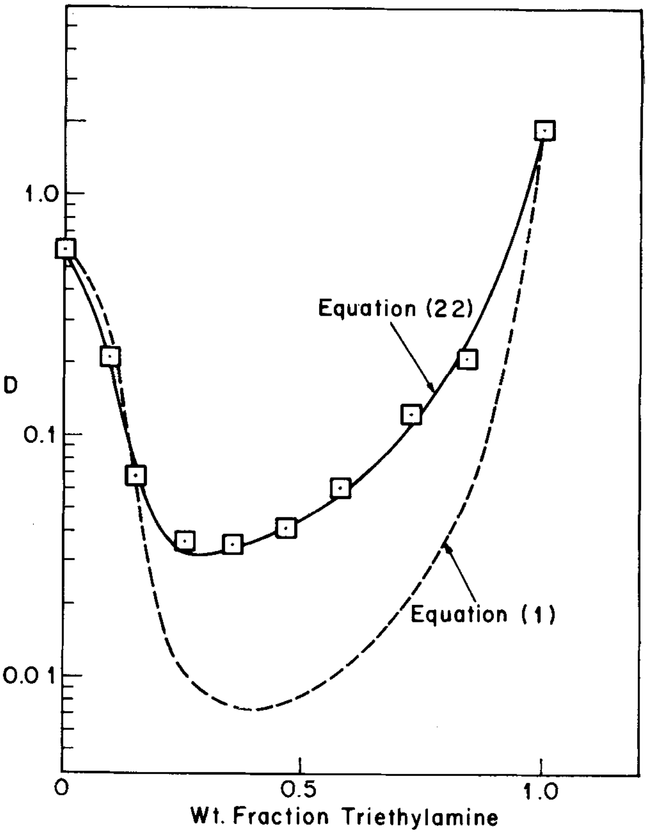

Figure 3. Predicted diffusion in triethylamine-water at 15°C: Cluster diffusion arguments (solid line) accurately predict the results. Conventional activity corrections (dashed line) are much less successful.

Other examples of diffusion near the consolute point are less conclusive. Measurements of laser-Doppler light scattering on isobutyric-acid water near its upper consolute point agree with theories of critical phenomena equivalent to Equation (21) (Chu et al 1969), but these measurements are limited to five determinations of D, without measurements of D_0 or of $\partial\mu_1/\partial x_1$. Interferometric measurements of diffusion of nitrobenzene-hexane near its upper consolute point are much more complete (Haase and Siry 1968). These are complemented by vapor pressure determinations and sedimentation experiments. While the experiments do not show the anomalous behavior observed in other systems (Block et al 1977), they do pro-

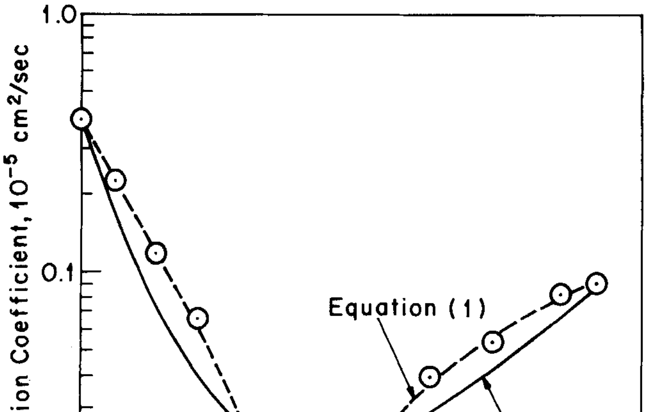

Figure 4. Predicted diffusion in nitrobenzene-hexane at 27°C: While cluster diffusion arguments are qualitatively successful (solid line), the conventional activity corrections are more accurate (dashed line). Data are from Haase and Siry (1968).

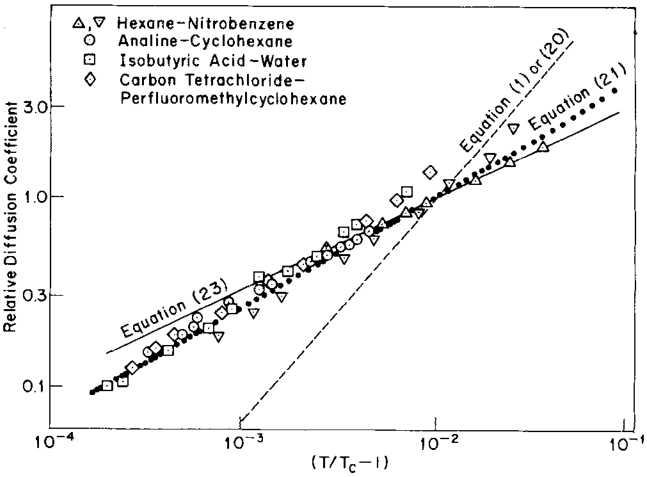

Figure 5. Diffusion vs. temperature, near consolute points: The critical point theories (dotted line) fit the results very closely. The cluster diffusion approach (solid line) is much more successful than the conventional prediction (dashed line). △, Claersson and Sundelöf (1957), ▽, Haase and Siry (1968), ○, Berge and Volochine (1968), □, Chu et al. (1968) ◇, Thiel et al. (1975).

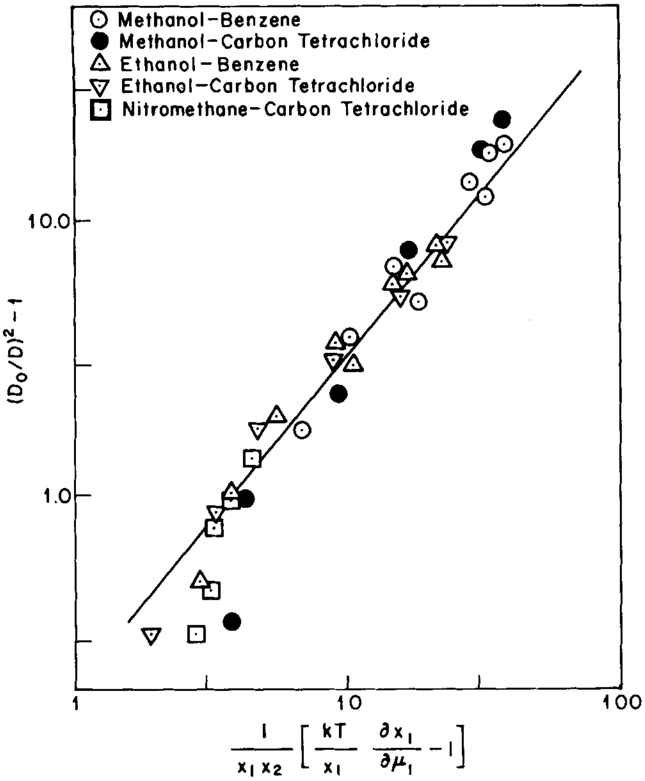

Figure 6. Diffusion in concentrated non-ideal solutions: This correlation, an analogue to Figure 2 but far from the consolute point, is consistent with Eq. (22) and hence with cluster diffusion in these systems. ○, Anderson et al. (1958), ●, Anderson and Babb (1963), △, Anderson et al. (1958), ▽, Hammond and Stokes (1956) and Anderson and Babb 1963, □, Miller and Carmen (1959).

vide one way of estimating D_0. On this basis, plots like Figure 2 can be prepared from which $K = 0.5$. The variation of diffusion with concentration can be predicted, as shown in Figure 4. This prediction is reasonable; however in this case, predictions based on Equations (1) or (20) are much superior.

More definite evidence in favor of cluster diffusion comes from the variation of diffusion with temperature shown in Figure 5. Equation (21), derived to apply at the consolute point, fits the data very closely. Equation (23), for cluster diffusion, fits much more closely than Equation (1) or (20), the conventional activity corrections. For this case, cluster diffusion definitely gives a more accurate picture.

This smaller temperature dependence suggested by Equations (21) and (23) has an interesting practical implication. Since diffusion is very slow in the region near the consolute point, liquid-liquid extractions could be difficult to effect, if this region were extensive. In fact, this region is small. Equations (21) and (23) correctly predict this: For a consolute point around room temperature, diffusion drop more than an order of magnitude only within about 3°C of the consolute point itself. Equations (1) and (20) are less successful: for example, Equation (20) predicts this temperature increment is about 30°C. If the region were in fact this big, consolute behavior might sharply affect industrial separation.

NON-IDEAL SOLUTIONS

To test the ideas developed above in less exotic situations, we focus on two previous theories of concentration dependent diffusion, those of Vignes (1968) and Kasanovich and Cullinan (1976). The former is chosen because of its unusual scope and wide success. The latter is included because it hints at empirical results like those developed theoretically.

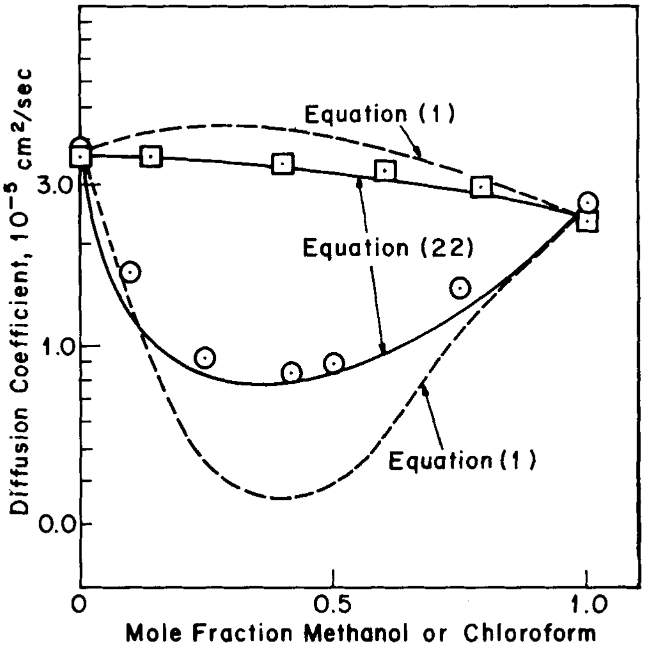

Figure 7. Predicted diffusion in concentrated non-ideal solutions: As in Figure 3, the cluster diffusion predictions (solid lines) are more successful than the conventional activity corrections (dashed line); these latter tend to be too large.

The Vignes theory estimates values of D_0 as a geometric average

$$D_0 = (D_{0,1m2})^{x_2}(D_{0,2m1})^{x_1} \qquad (26)$$

where $D_{0,imj}$ is the diffusion coefficient of species "i" in excess species "$j \neq i$." Vignes combined these estimates with a linear activity correction like that in Equation (1). When the activity correction was small, he obtained reasonable results. When it was large, he was less successful.

We decided to test Equation (22) for five systems for which Vignes found his theory inadequate. The results, shown in Figure 6, again show that the inverse square of the diffusion coefficient varies with the activity correction. All five of these systems are miscible in all proportions; all show major deviations from ideality; only one (nitromethane-carbon tetrachloride) is close to its consolute point.

Results in Figure 6 support the variation suggested by Equation (22). They give a value of 0.5 for the constant K, near that found for nitrobenzene-hexane and about five times greater than those found for triethylamine-water. To see if these values are reasonable, we return to the definition of K, which is $(1/16\ \pi r_0^2 an)$. The quantity a is on the order of r_0; and n is probably about $[4/3\ \pi(2r_0)^3]^{-1}$. Thus K should be about 2/3, in reasonable agreement with the measured value. The predictions of concentration-dependent diffusion obtained are exemplified by those in Figure 7. Equation (22) does a better job. Equation (1) predicts too large a variation of the diffusion coefficient.

The Kasanovich-Cullinan theory (1976) provides additional support for Equation (22). This theory calculates D_0 as a type of volume average

$$D_0 = D_{0,2m1}\,\phi_1 + D_{0,1m2}\,\phi_2 \qquad (27)$$

where the ϕ_i's are modified volume fractions (Hildebrand 1977). This theory searches for an empirical relation between D/D_0 and $(\partial\mu_1/\partial x_1)$ for five chemical systems different than those in Figure 6. These authors then make a plot equivalent to Figure 6 (their Fig. 2) and obtain an equivalent result, that diffusion varies with the square root of $(\partial\mu_1/\partial x_1)$, and not with the first power suggested by Equation (1).

Thus Vignes (1968) and Kasanovich and Cullinan (1976) support Equation (22) and the concept of cluster diffusion, especially for highly non-ideal solutions. However, such a concept will not always be valid, especially for near-ideal solutions where long-range repulsive forces exist between solute molecules. The obvious example is dilute salt solutions, where Equation (1) is well verified (e.g., Robinson and Stokes 1959). The reason is almost certainly that electrostatic forces reduce any fluctuations in solute concentration. In addition, the concept of cluster diffusion is presently compromised by the constant K and by the uncertain averages for D_0. Both K and D_0 deserve further investigation.

ACKNOWLEDGMENTS

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NOTATION

a, a_{ij} = characteristic length (Equations 10, 14)
a_i = activity of species "i"
A, B = van Laar solution parameters (Equation 18)
D = diffusion coefficient
$D_0, D_{0,imj}$ = reference value of diffusion coefficient
$F(r)$ = time-integrated velocity correlation function (Equation 6)
$G(r)$ = concentration correlation function (Equation 8)
k = Boltzmann's constant
K = constant (Equation 22)
n = number molecules per volume (Equation 13)
r = radial distance
r_0 = effective molecular radius
T = temperature
x_i = mole fraction species "i"
Z = phenomenological coefficient (Equation 5)
δ = critical exponent (Equation 12)
η = viscosity
μ_i = chemical potential species "i"
v = critical exponent (Equation 12)
ξ, ξ_{ij} = correlation length (Equation 10)
ϕ_i = volume fraction
ω = regular solution parameter (Equation 2)

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Analysis of the Phase Inversion Characteristics of Liquid-Liquid Dispersions

Correlations of the collision frequency and the coalescence frequency of an agitated dispersion are combined with models relating drop sizes and hold-up to agitator speed, to predict the ambivalence range and phase inversion composition of liquid-liquid dispersions. Our model was tested by comparing predicted and experimental phase inversion compositions of the systems toluene-water and carbon tetrachloride-water. In addition, the predicted results have been compared with published results for the system kerosene-water, and in all cases, agreement between predicted and experimental results are excellent.

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SCOPE

Liquid-liquid dispersions are generated in solvent extraction operations, direct contact heat exchangers and in two-phase chemical reactors. The identification of the dispersed phase under all conditions and the limits of stability of these heterogeneous mixtures are most important in these process operations. Hitherto, the limits of the ambivalence range and the phase inversion concentrations have been treated qualitatively, and there has been no attempt to predict either limit or assess the effect of agitator speed and the physical properties of the system on the inversion characteristics. In this article, phase inversion is analyzed in terms of the collision frequency and coalescence frequency of agitated dispersions. It was possible to combine models of these two phenomena with the effects of disperse phase hold-up on drop size, to accurately predict the ambivalence range and the phase inversion compositions.

CONCLUSIONS AND SIGNIFICANCE

The collision frequency and the coalescence frequency of agitated dispersions have been studied extensively, and both have been found to depend on the turbulence level of the agitation, the disperse phase hold-up, and the physical properties of the system. These phenomena can be combined to accurately predict the ambivalence range and the phase inversion concentration. Thus the ambivalence range can vary from 20% dispersed to 90%, depending on how the dispersion was produced. Recently, Arnold (1975) showed that a solvent extractor operates most efficiently under sequential phase inversion conditions. Therefore, it is necessary to be able to predict the ambivalence range and the phase inversion concentrations, and the model presented here has been tested on two systems of widely different physical properties, together with a third studied qualitatively by another researcher (Ali 1969). We found that the ambivalence range and the phase inversion concentration can be predicted accurately as a function of agitator speed, dispersed phase hold-up and the physical properties of the system. This has significance in the design and operation of extraction equipment, direct contact heat exchangers, and two-phase liquid-liquid reactors.

Characterization of a liquid-liquid dispersion is an important requirement in many industrial chemical engineering operations such as solvent extraction, direct contact heat exchangers, and batch and continuous heterogeneous reactors. These dispersions are produced by injecting one phase through a distributor into the second phase, or mechanically agitating the two phases in the equipment in

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