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Investigation of the Thermodynamic Behavior of the System, Acetone-Carbontetrachloride, by the Equilibrium Sedimentation Technique

The equilibrium sedimentation technique for the direct determination of the chemical potential composition derivatives of a liquid mixture is applied to the binary system acetone-carbontetrachloride. Equilibrium concentration profiles obtained in an ultracentrifuge are used with the Wilson equation to quantitatively determine the composition variation of the activity coefficients over the entire range of composition. Results agree well with previous data and indicate the technique to be accurate and reliable.

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SCOPE

The phenomenon of sedimentation equilibrium, although well understood (Fujita, 1962), has only recently been proposed (Cullinan, 1968) as a basis for a practical experimental technique for the determination of liquid solution thermodynamic properties. The objective of this paper is the experimental determination of the composition variation of the activity coefficients of the binary liquid system acetone-carbontetrachloride at 20°C. over the entire range of composition.

The technique involves the measurement of equilibrium composition profiles established in an ultracentrifuge. From these profiles the variation of solution activity with composition is calculated from the governing thermodynamic condition of uniformity of total chemical-mechanical potential.

CONCLUSIONS AND SIGNIFICANCE

Comparison of the results with the best existing data indicates that the equilibrium sedimentation technique is a reliable and accurate method for the determination of liquid solution activity coefficients. The method offers several distinct advantages over conventional vapor-liquid equilibrium techniques. First, the method permits the characterization of the entire composition range with a small number of experiments. Second, the method gives a direct measure of the composition variation of solution activity. Finally, the equilibrium sedimentation technique is directly applicable to the determination of the composition variation of the activity coefficients of multicomponent liquid systems.

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Recent developments in predicting diffusion coefficients (Cullinan and Cusick, 1967; Leffler and Cullinan, 1970; Vignes, 1966) are found dependent on the knowledge of the chemical potential composition derivatives. Most workers have obtained the chemical potential composition derivatives for computing the thermodynamic correction to the diffusion coefficient (the thermodynamic factor) by differentiating activity coefficient data. Activity coefficients are usually obtained using vapor-liquid cells. Differentiation of such data involves certain error, hence direct determination is desirable.

Cullinan (1968) applied the equilibrium sedimentation theory for evaluating the chemical potential composition derivatives by relating them to the equilibrium composition distribution. Further studies by Cullinan and Lenczyk (1969) were aimed at verifying the consistency of the theory when applied to binary and multicomponent systems.

The present work, which makes use of the theories presented by Cullinan and Lenczyk (1969) is directed at measurement of the thermodynamic factor in a direct manner. The approach is tested using the acetone-carbontetrachloride system.

THEORY

The general principles of irreversible thermodynamics can be applied to the case of a liquid system subjected to a centrifugal field. The equilibrium distribution for a binary system is governed by (Cullinan and Lenczyk, 1971)

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)\frac{dx_1}{dr} = (M_1 - \rho\overline{V}_1)\omega^2 r \tag{1}$$

and the time to reach a given degree of equilibrium with an initially uniform system is obtained from (Cullinan and Lenczyk, 1969)

$$t_\delta = \frac{(\Delta R)^2}{4\,\Pi^2 D}\ln\frac{2}{\Pi^2(1-\delta)} \tag{2}$$

At a time corresponding to $\delta = 0.99$, the system should essentially be at equilibrium.

APPARATUS AND PROCEDURE

The experimental investigation was conducted in a model L Beckman ultracentrifuge equipped with a type 50 titanium swinging bucket rotor. The rotor assembly consisted of three stainless steel tubes held in buckets arranged symmetrically with respect to the axis of rotation. The curvature at the bottom of the tubes was eliminated by using epoxy hemispheres so that the cells could be considered essentially cylindrical.

The centrifuge was equipped with fine speed and temperature controls. The variation in speed was found to be of the order of 0.1%. The temperature was checked by lowering a thermocouple into the cells after a run. Potentiometric measurements indicated that the temperature was nearly uniform, a gradient of 1.2°C. being observed.

The runs were conducted at 20°C. The rotor of the centrifuge was operated in a vacuum to reduce frictional heat generation. Refrigeration was used to stabilize the temperature during a run.

Several experiments were conducted using various starting concentrations so that the entire composition range could be studied. All the equilibrium runs were made at the same speed of 30,000 rev./min. and were of 240 hours duration. This time is 45% larger than $t_{0.99}$ calculated from Equation (2) using the minimum value of the diffusion coefficient of the acetone-carbontetrachloride system (Anderson et al., 1958).

The sampling procedure established was fairly simple in nature. At the end of the run the buckets were detached from the rotor and secured upright in a holder. A syringe was then lowered into the tubes, and a certain amount of liquid was removed and stored in a 5 ml. vial. Subsequent samples were obtained in a cyclic pattern so as to include all the buckets.

The radial position of the samples was determined in a stepwise manner. The radius corresponding to the bottom of the cell had been quoted by the manufacturer and was used as a starting point in the calculations. The heights corresponding to the volumes of liquid removed were evaluated. The radial position was then taken to be the geometric mean of the radii corresponding to the outer surfaces. This mean was based on an approximate solution of Equation (1) which shows the equilibrium composition to be proportional to the square of the radial position.

Extreme care is necessary during the sampling procedure in order to prevent systematic error. Previous work (Cullinan and Lenczyk, 1969, 1971) shows that the sampling procedure is accurate and reproducible with a minimum of systematic error. In addition, the short sampling time required results in a negligible effect of back diffusion.

The liquid samples obtained were analyzed using gas chromatography. A Hewlett Packard F and M Model 5750 gas chromatograph equipped with a thermal conductivity detector was used for the purpose. The chromatograph was coupled to a digital integrator, and the areas corresponding to the recorded peaks were directly obtained as the integrator output. The column of the chromatograph was packed with 5% dinonyol phthalate on chromosorb W. Helium was used as the carrier gas. Calibration and analysis were conducted simultaneously.

ANALYSIS OF DATA

The objective of the calculations was to obtain the chemical potential composition derivative as a function of composition over the entire concentration range.

Cullinan and Lenczyk (1969) used an integral analysis making the basic assumption that the factor $(M_1 - \rho\overline{V}_1)/(\partial\mu_1/\partial x_1)$ is constant. Integrating Equation (1) they obtained

$$x_1 - x_{10} = \frac{M_1 - \rho\overline{V}_1}{\partial\mu_1/\partial x_1}\,\frac{\omega^2}{2}\,(r^2 - R_0{}^2) \tag{3}$$

A plot of x_1 against r^2 was found to be linear in their case, the chemical potential derivatives being determined from the value of the slope. In general, Equation (3) is an approximation which, for a given system, is only valid if the resulting composition changes are sufficiently small.

This analysis is not suitable for the acetone-carbontetrachloride system. Density and thermodynamic data (Timmermans, 1959; Vignes, 1966) indicate that $(M_1 - \rho\overline{V}_1)/\partial\mu_1/\partial x_1$ varies by about 12% over the range of composition encountered in these experiments.

In order to circumvent the problems posed by the integral method an analysis making use of Wilson's thermodynamic model (Wilson, 1964) for a binary solution was attempted. An optimization technique was used to obtain the best values of the Wilson parameters. In this application the function to be minimized is the error sum of squares calculated from the fit of the Wilson equation to the given set of data.

The use of the Wilson model is superior to a differential analysis based on the direct solution of Equation (1) for the desired quantity $\partial\mu_1/\partial x_1$. This is so because the slight scatter in the x versus r data produces a fair amount of uncertainty in the point estimates of the gradient dx_1/dr.

It should also be pointed out that, although a modest pressure gradient is established in the cell, the thermodynamic pressure correction (Cullinan and Lenczyk, 1969) for systems of the present type, which exhibit only small volume change on mixing, is negligible. Thus, a single unique set of Wilson parameters applies, and these are essentially the same as the values at 1 atm.

Now the chemical potential of a component in a binary can be written as

$$\mu_1 = \mu_1^0 + RT \ln \gamma_1 x_1 \tag{4}$$

The chemical potential composition derivative can thus be related to the composition derivative of the activity coefficient according to the relation

$$\frac{1}{RT}\frac{\partial \mu_1}{\partial x_1} = \frac{1}{x_1} + \frac{d \ln \gamma_1}{dx_1} \tag{5}$$

The Wilson expression for the activity coefficient of a component in a binary solution is given by (Wilson, 1964)

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \tag{6}$$

The equation has two adjustable parameters Λ_{12} and Λ_{21}. In Wilson's derivation (*11*) these are related to the pure component molar volumes and to characteristic energy differences. Using Equations (5) and (6)

$$\frac{1}{RT}\frac{\partial \mu_1}{\partial x_1} = \frac{1}{x_1} + \frac{\Lambda_{12} - 1}{\{x_1(1 - \Lambda_{12}) + \Lambda_{12}\}} - \frac{\Lambda_{12}}{\{x_1(1 - \Lambda_{12}) + \Lambda_{12}\}^2} + \frac{\Lambda_{21}}{\{x_1(\Lambda_{21} - 1) + 1\}^2} \tag{7}$$

Now according to Equation (1)

$$\frac{1/RT \dfrac{\partial \mu_1}{\partial x_1}}{(M_1 - \rho V_1)}\, dx_1 = \omega^2\, r dr \tag{8}$$

Integration of Equation (8) over a finite range r_a to r_b where the concentration changes from x_{1A} to x_{1B}, the left-hand side could be computed after substituting Equation (7).

$$\int_{x_{1A}}^{x_{1B}} \frac{1/RT \dfrac{\partial \mu_1}{\partial x_1}}{(M_1 - \rho V_1)}\, dx_1 = \phi(\Lambda_{12}, \Lambda_{21}, x_{1A}, x_{1B}) \tag{9}$$

where the density ρ is given by

$$\rho = \frac{x_1 M_1 + (1 - x_1) M_2}{x_1 V_1 + (1 - x_1) V_2} \tag{10}$$

The right-hand side of the integrated equation is

$$\frac{\omega^2}{2}(r_b^2 - r_a^2) = \psi(r_a, r_b) \tag{11}$$

The error function to be minimized was thus formulated as

$$F = \Sigma(\psi - \phi)^2 \tag{12}$$

the summation being performed using successive pairs of points on the equilibrium distribution curve. The composition distribution for each experiment was obtained by smoothing out the experimental data. This was done making a least squares fit using a polynomial approximation. The 95% confidence limits associated with the equilibrium profiles were also established.

A number of experiments with different initial compositions were performed so as to encompass the entire composition range. The Wilson parameters for the system were obtained by an optimum fit of all the data. In this composite analysis the error function of Equation (12) was defined to be the net sum of the several functions. From the individual experiments, the consistency of the values was checked by back calculating composition profiles to determine whether they were within their respective confidence envelopes.

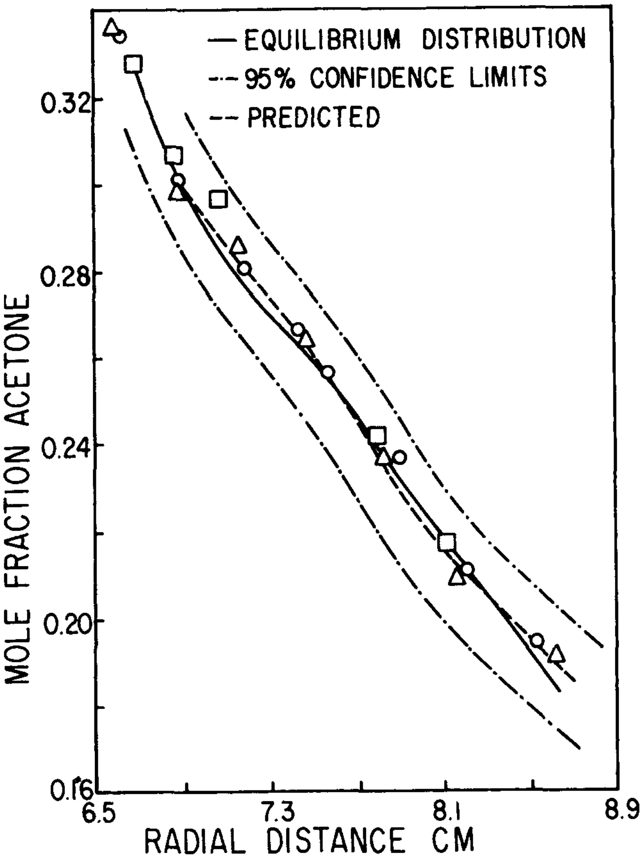

Fig. 1. Equilibrium profile $x_{A0} = 0.25$.

DISCUSSION OF RESULTS

The Wilson parameters obtained from the composite analysis are

$$\Lambda_{12} = 0.3382$$
$$\Lambda_{21} = 0.8665$$

The consistency of these values was checked by back calculating composition profiles. Typical results are presented in Figure 1. All such plots are found to lie well within the 95% confidence envelopes. This agreement is further confirmation that a single unique set of Wilson parameters applies under the experimental conditions. In the figure the different symbols on the equilibrium distribution characterize samples obtained from various cells.

The activity coefficient values arrived at by substitution of Λ_{12} and Λ_{21} into the Wilson equation is compared with the data of Brown and Smith (1957) in Figure 2. The mean deviation is 4.5% and can be attributed to the temperature dependence of the activity coefficient. The present data obtained at 20°C. is expected to yield higher values since Brown and Smith conducted their experimentation at 45°C.

The thermodynamic factor α is given by

$$\alpha = 1 + \frac{d \ln \gamma_1}{d \ln x_1} \tag{13}$$

Using Equation (13)

$$\alpha = 1 + x_1 \left\{ \frac{1}{RT} \frac{\partial \mu_1}{\partial x_1} - \frac{1}{x_1} \right\} \tag{14}$$

The values of α obtained from Equation (14) were compared with the data from Vignes (1966) in Figure 3. The mean deviation over the entire range of composition is less than 6%. This is also ascribed to the variation of α with temperature, since Vignes' derived his data from that of Brown and Smith.

CONCLUSION

The application of the equilibrium sedimentation theories to the study of the solution thermodynamics of the acetone-carbontetrachloride system has been explored. The activity coefficient values, determined using the Wilson equation, were found to compare satisfactorily with existing data. This validated the approach, which was primarily aimed at evaluation of the thermodynamic factor α without differentiating activity coefficient data.

The analysis was constructed in a manner so that it could be easily extended to complete characterization of multicomponent systems. The Wilson expression for multicomponent solutions is dependent on the knowledge of binary interaction parameters. A few experiments, as demonstrated here, are sufficient for investigating the entire range of composition for a binary.

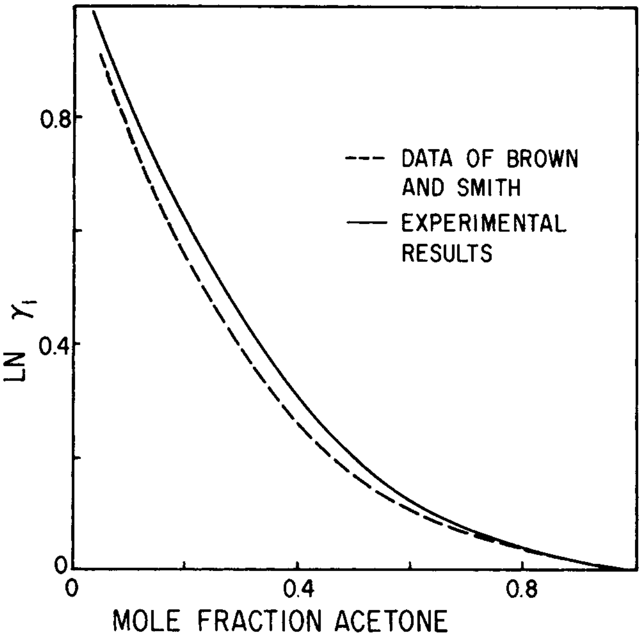

Fig. 2. Activity coefficient results.

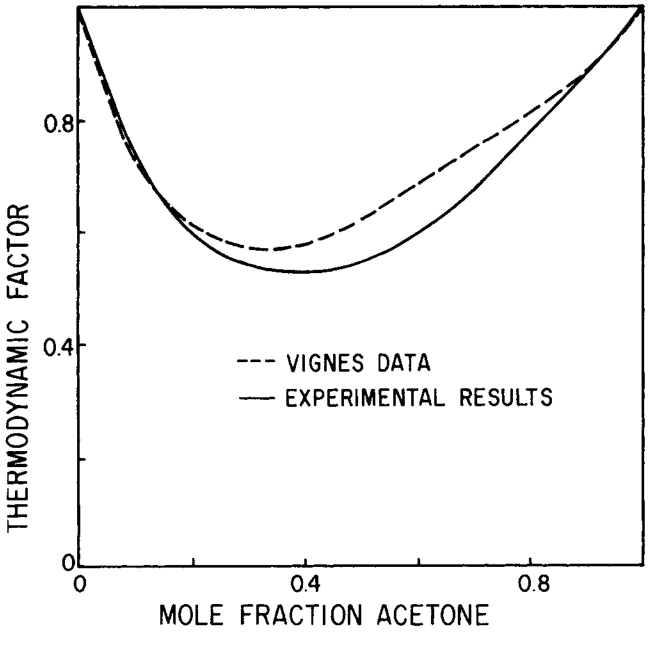

Fig. 3. Thermodynamic factor results.

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NOTATION

D = binary diffusion coefficient
M_k = molecular weight of species k
r = radial distance
R_i = radial position of the boundaries of the cell i = 1, 2
ΔR = radial length of the cell, $R_2 - R_1$
t = time
T = temperature
$\bar{V}_k$ = partial molal volume of component k
x_k = mole fraction of species k

Greek Letters

α = thermodynamic factor defined by Equation (13)
γ_k = activity coefficient of species k
δ = fractional approach to equilibrium
μ_k = chemical potential of species k
ρ = density of solution
ω = angular velocity
Λ_{12}, Λ_{21} = Wilson parameters for the binary solution

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