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The Diffusion Coefficients and Viscosities of the $UO_2(NO_3)_2 \cdot 2TBP$ Complex in Organic Solvents

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Abstract

The diffusion coefficients and the solution viscosities of the $UO_2(NO_3)_2 \cdot 2TBP$ complex in 12 solvents (tributylphosphate, n-hexane, n-dodecane and 9 mixed solvents) at 298 K were determined by use of an analytical ultracentrifuge and an Ubbelohde viscometer. It is shown in the mixed solvents that all systems obeyed the Jones–Dole relation. The product of diffusion coefficient and viscosity is roughly constant, corresponding to an Einstein–Stokes radius of 0.54 nm for the uranium complex.

Introduction

This work is part of a series of investigations of diffusion in aqueous and non-aqueous systems from which it is hoped that information on the relation between diffusion coefficients and other properties of the solutions may be obtained. Since the transport data of uranylnitrate were urgently needed to optimize nuclear fuel reprocessing, the measurements were carried out in tributylphosphate (TBP) acting as a solvent and complexing agent [1]. The hydrocarbons n-hexane, n-dodecane and a relevant mixture of n-C_{10}–C_{13}, which has been used in the Purex process, were added in different quantities as diluents, because of the high viscosity of pure TBP. In those different solvent systems the diffusion studies should be capable of yielding information about the nature of the kinetic entities of the uranium complex. For this purpose, however, it is necessary to measure the concentration dependence of the diffusion coefficient of uranium in order to extrapolate to infinite dilution, since the theory of diffusion at high concentrations requires knowledge of the activities of the solute which, in general, is not available. In the present investigation an analytical ultracentrifuge was used to monitor the diffusion characteristics with the aid of both the Schlieren and absorption (at 425 nm) optical systems [2, 3].

On the other hand viscosity measurements give an insight into the structure of the solution [4]. Therefore, in aqueous and non-aqueous solutions the concentration dependence of the viscosity has been studied extensively. In most cases the data obtained can be interpreted in terms of the semi-empirical Jones–Dole equation

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc$$

where η and η_0 stand for the solution and solvent viscosities and c for the concentration. A and B are adjustible parameters. This equation has been found valid to approximately 0.1 M. At higher concentration, a term being quadratic in concentration, may be added. The square root term A has significant theoretical interest in relation to ion–ion interactions and can be calculated theoretically. Unfortunately, the limiting ionic conductivities which are required for the calculations are not yet available. The B coefficient of the Jones–Dole equation is useful parameter for interpreting ion–solvent interactions. Qualitatively, it can be described by the Einstein equation

$$B = 2.5\ v/c$$

where v is the volume occupied by the ions per milliliter of solution. This equation predicts that the presence of ions should increase the solution viscosity proportional to their size. There is no satisfactory way of calculating the B coefficient. In reviewing investigations made on aqueous solutions it has been used to describe certain ions as 'structure makers', where they exhibit B values [5, 6]. If there are uncertainties being due to the thermodynamic properties of the solutions they will be eliminated by extrapolating to infinite dilution.

The radius, r, can be determined by the well-known Einstein–Stokes relation

$$D = kT/6\pi\eta r$$

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using the limiting diffusion coefficients and the viscosity of the pure solvent. The only doubt still remaining concerns the validity of using Stokes law for the frictional force on the particle when the solvent consists of discrete molecules of size comparable with that of the solute.

Experimental

For the preparation of the $UO_2(NO_3)_2 \cdot 2TBP$ complex two methods were used. In the first, excess solid uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$, was added to pure tributylphosphate, TBP, after which the water of crystallization was decanted off and the organic phase dried over a molecular sieve [7]. Solutions were then prepared gravimetrically by weighing known quantities of the complex into the solvents. In the second method, a series of TBP-solvent solutions of differing TBP concentrations were prepared gravimetrically after which excess solid uranyl nitrate was added and the resulting solutions dried as before.

The following complexonometric titration method was used in order to establish the ratio of TBP to uranyl nitrate which has been reported to be 2:1 in this complex. A known quantity of the solution, approximating to an equivalent of 25 mg of uranium was pipetted into a flask and contacted with 10 cm^3 of bidistilled water. The solution was stirred continually and 0.5 g of ascorbic acid were added. The pH was adjusted to 3.0 ± 0.5 by the addition of 1 M sodium hydroxide solution. 0.1 g of sodium hydrosulfite and 0.5 cm^3 of freshly prepared 0.1% methyl thymol blue were then added. This solution was titrated with 0.004 M EDTA-Na_2 solution until a pale blue colouration was obtained after which 5 cm^3 of 0.4% potassium meta periodate solution was added whereupon the solution returned to dark blue. After waiting for two minutes for all the residual six-valent uranium to be reduced, the solution was titrated with EDTA until a yellow colouration was obtained. Results indicated that the concentration determined by this complexonometric titration were in excellent agreement with theoretical values assuming the formation of the $UO_2(NO_3)_2 \cdot 2TBP$ complex in the saturated test solutions.

The measurements were carried out at a temperature of (25.00 ± 0.01) °C. Diffusion coefficients were measured with the aid of a Beckman Instruments Ltd. 'Model E' analytical ultracentrifuge. A capillary type double-sector cell was used, consisting of two compartments which could be filled separately with test solution and solvent. The cell was fitted into a rotor and accelerated to a final measurement velocity of 5200 r.p.m., whereby an artificial boundary was created by overlaying the test solution with solvent. The values of the diffusion coefficients, being correct to within ±3%, which are presented in this work, are the mean values of those obtained by both the Schlieren and absorption (425 nm) optical systems.

Viscosities were determined by a Schott Ltd. 'AVS' instrument using a calibrated Ubbelohde-type viscometer. As a consequence of the long flow-times (400–700 s), which were reproducible to 0.1 s, the kinetic energy correction was neglected and the viscosities were calculated from the flow-times and densities.

Densities were measured by a digital densitometer and are accurate to the 4th decimal place, using air and bidistilled water for calibration.

Results and Discussion

The viscosities and densities of $UO_2(NO_3)_2 \cdot 2TBP$ in pure dodecan, pure TBP, 30/70 TBP/C_{12} and 30/70 TBP/C_{10}–C_{13} are listed in Table I. As expected, the solution densities and viscosities are higher, when containing the uranyl nitrate–tributylphosphate complex. In the plot of $(\eta/\eta_0 - 1)/c^{1/2}$ against $c^{1/2}$, the slope of the straight lines corresponds to the viscosity B coefficient. The results indicate that the Jones–Dole equation is valid for the mixed solvents up to $c = 0.1$ M, for pure TBP solution it is valid, at least, up to $c = 0.06$ M. As the densities are linear in their dependence on the concentration of the complex, the slope m was calculated according to $\rho_3 = \rho_1 + mc$, where ρ_3 and ρ_1 stand for the densities of the solution and of the solvent. The values of the slope m for the different systems are listed in Table III together with the viscosity B coefficients.

Usually, the B coefficient is believed to have two origins. The first is the disruption of the hydrodynamic streamlines due to the effective size of the solute particle in solution; the second is any specific electrostatic effect the ions may have on the viscosity of the solvent. The value of B may be either positive or negative and it appears to be an additive property of the ions. For dilute aqueous electrolyte solutions, the ions which exhibited positive B values could be described as 'structure makers' and those ions exhibiting negative B values as 'structure breakers'.

Some authors considered the relation between viscosity and concentration in non-aqueous systems should be simpler because the complications due to water structure were excluded, and it would be still reasonable to discuss the 'structure maker' and 'structure breaker' in a similar way, taking the solute molecules instead of ions and ignoring the electrostatic effect [8]. According to the positive values of B (see Table III) it is evident that in the solution $UO_2(NO_3)_2 \cdot 2TBP$ is a strong 'structure maker'.

Viscosity B coefficient can also be interpreted by Einstein's equation on the assumption of the solute particles as idealized spheres in a continuum. This equation predicts that the presence of ions should

TABLE I. Viscosity and Density of $UO_2(NO_3)_2 \cdot 2TBP$ in Different Solvents

In Dodecane					
$c \times 10^2$ (g cm^{-3})	0.78	1.54	4.36	6.21	8.71
ρ (g cm^{-3})	0.7485	0.7522	0.7660	0.7749	0.7870
η (cP)	1.360	1.375	1.430	1.467	1.519
In 30/70 TBP/C_{12}					
$c \times 10^2$ (g cm^{-3})	0.97	1.77	2.78	4.70	7.61
ρ (g cm^{-3})	0.8033	0.8061	0.8097	0.8166	0.8270
η (cP)	1.594	1.612	1.632	1.673	1.733
In 30/70 TBP/C_{10}-C_{13}					
$c \times 10^2$ (g cm^{-3})	1.76	3.52	5.37	7.14	8.99
ρ (g cm^{-3})	0.8030	0.8092	0.8159	0.8222	0.8288
η (cP)	1.486	1.519	1.554	1.589	1.626
In TBP					
$c \times 10^2$ (g cm^{-3})	1.60	2.49	3.20	4.88	8.09
ρ (g cm^{-3})	0.9780	0.9811	0.9835	0.9892	0.9999
η (cP)	3.404	3.445	3.481	3.563	3.748

TABLE II. Diffusion Coefficients (D) of $UO_2(NO_3)_2 \cdot 2TBP$ in Different Solvents

In Dodecane						
$c \times 10^2$ (M)	0.43	0.85	1.53	3.72	5.98	8.05
$D \times 10^6$ (cm^2 s^{-1})	2.98	2.96	2.92	2.90	2.71	2.55
In 30/70 TBP/C_{12}						
$c \times 10^2$ (M)	0.49	0.99	3.04	5.29	6.41	7.91
$D \times 10^6$ (cm^2 s^{-1})	2.59	2.63	2.58	2.60	2.52	2.41
In 30/70 TBP/C_{10}-C_{13}						
$c \times 10^2$ (M)	1.27	2.05	4.17	6.35	7.30	9.45
$D \times 10^6$ (cm^2 s^{-1})	2.79	2.78	2.81	2.78	2.81	2.71
In 30/70 TBP/C_6						
$c \times 10^2$ (M)	0.92	1.86	3.84	4.86	6.71	8.72
$D \times 10^6$ (cm^2 s^{-1})	7.31	7.04	7.17	6.92	6.78	6.37
In TBP						
$c \times 10^2$ (M)	0.48	0.86	1.26	1.73	2.63	3.09
$D \times 10^6$ (cm^2 s^{-1})	1.08	1.05	1.08	0.97	0.99	0.96

TABLE III. Viscosity Coefficient (B) and Density Coefficient (m) of $UO_2(NO_3)_2 \cdot 2TBP$ in Different Solvents

Solvent	B (cm^3 g^{-1})	m
Dodecane	1.55	0.4856
30/70 TBP/C_{12}	1.37	0.3574
30/70 TBP/C_{10}-C_{13}	1.38	0.3573
TBP	1.49	0.3373

increase the solution viscosity which is proportional to the ionic size. For the non-aqueous solutions, a similar relation between B and the radius of the solute molecule should exist. Therefore, it is expected that relative high B values for the solutions under discussion could be obtained, because the size of the $UO_2(NO_3)_2 \cdot 2TBP$ complex is greater than that of any solvent molecule in the above mentioned experiments. Indeed, as the results show, the B values of these solutions as determined here, are greater than

TABLE IV. Diffusion Coefficient (D) and Radius (r) of $UO_2(NO_3)_2 \cdot 2TBP$ in Different Solvents and Viscosity and Density of the Solvents

Solvent	ρ_1 (g cm^{-3})	η_0 (cP)	$D_0 \times 10^6$ (cm^2 s^{-1})	$r \times 10$ (nm)
n-Hexane	0.6567	0.307	13.30	5.30
30/70 TBP/n-Hexane	0.7289	0.471	7.70	6.00
60/40 TBP/n-Hexane	0.8205	0.815	4.80	5.60
n-Dodecane	0.7447	1.347	3.00	5.40
30/70 TBP/C_{10}-C_{13}	0.7967	1.455	2.80	5.36
30/70 TBP/n-Dodecane	0.7998	1.576	2.60	5.33
50/50 TBP/n-Dodecane	0.8408	1.825	2.22	5.39
60/40 TBP/n-Dodecane	0.8628	1.993	2.05	5.34
70/30 TBP/n-Dodecane	0.8888	2.225	1.82	5.39
80/20 TBP/n-Dodecane	0.9147	2.495	1.59	5.50
90/10 TBP/n-Dodecane	0.9421	2.856	1.30	5.88
TBP	0.9727	3.329	1.10	5.96

the typical B values of solutions with comparably small solute molecules.

Viscosity A coefficient is attributed to the interionic electrostatic forces. Jones and Dole summarized that the value A is negative for all strong electrolytes and is zero for non-electrolytes. As $UO_2(NO_3)_2$ is usually a weak electrolyte, low values A or even zero value A could be expected. In our experiment, the A values of the uranyl nitrate complex in pure TBP and in 30/70 TBP/C_{12} were -0.01 and in C_{12} and 30/70 TBP/C_{10}–C_{13} were -0.02. These A values, being quite near to zero, could be considered as a further information of the low dissociation of $UO_2(NO_3)_2 \cdot 2TBP$ complex at least in the investigated organic systems.

The differential diffusion coefficients D are given in Table II at a concentration c, which was calculated from $(c_1 + c_0)/2$, where c_1 and c_0 means the concentration of the complex in the solution and the solvent or a more diluted solution, respectively. In all systems at small concentrations the experimental data can be represented adequately by a linear relation between D and c. The extrapolated value at zero concentration is the limiting diffusion coefficient D_0.

In these non-electrolyte solutions no long-range forces are to be expected. Consequently the various factors known to effect the variation of diffusion coefficients with concentration will be approximately linear functions at the low concentrations used here. It should be noted that a solute–solute association would lead to a marked concentration dependence of D even in dilute solutions. Since this is not observed, the $UO_2(NO_3)_2 \cdot 2TBP$ complex should have a sufficient stability to diffuse as a distinct unit. Contrary to the results in the organic solvents, diffusion measurements of uranyl nitrate in aqueous solutions indicate a great concentration dependence showing even minima and maxima because of a change of ionic species due to different complex formations due to variation of the concentration [9].

The limiting diffusion coefficients of $UO_2(NO_3)_2 \cdot 2TBP$ and the viscosities of the organic solvents are given in Table IV together with the corresponding values of the Stokes radius r. It is evident from Table IV that there is a systematic decrease in the value of the diffusion coefficient with increasing viscosity. This is illustrated graphically in Fig. 1.

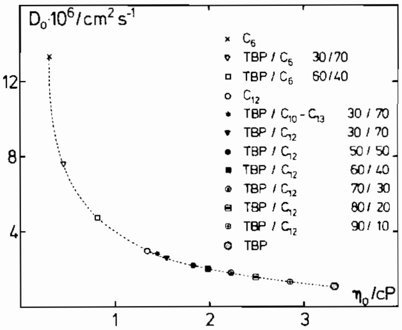

Fig. 1. Variation of the diffusion coefficient of the $UO_2(NO_3)_2 \cdot 2TBP$ complex with solvent viscosity.

The diffusion coefficient of a species may be related reciprocally to the frictional coefficient of the solute particle, whereas the viscosity may be related directly to the same frictional coefficient. The combination leads to the well-known Einstein–Stokes relation. If the diffusion coefficient and the viscosity are measured at the same temperature, the product of D_0 and η_0 will be reciprocal to the Stokes radius r

$$r = \frac{RT}{6\pi N \eta_0 D_0}$$

where R is the universal gas constant, T the absolute temperature and N Avogadro's constant. The moving particles are assumed to be spherical in shape ignoring the structure of the uranyl nitrate complex. As the Einstein–Stokes equation is only valid under certain conditions, it was proved heretofore that the moving particles were non-electrolytes and that their size was of a higher magnitude than that of the solvent. If the interactions between the solvent and the solute are neglected, the radius of the moving particle will be the same in each of the solvents used, indicating that there is no change in the species of the complex. It can be seen that in the mixed solvents the deviation of r from the mean is approximately 3% and in most cases this deviation is even lower, indicating the solvation of the uranyl nitrate–tributylphosphate complex to be minimal. It is concluded that this deviation is a result of experimental error in the measurement of the diffusion coefficient and that, for all the systems, the Einstein–Stokes relationship is obeyed.

A value of 0.54 nm has been calculated for the Stokes radius, which is in accordance with the model applied, though the numerical factor might be different because the shape of the complex is not spherical. Therefore it follows that it should be possible to calculate a value of the diffusion coefficient which is needed to optimize the extraction process for any relevant solvent mixture of this system. Knowing the viscosity of the solvent which can easily be determined, the desired diffusion coefficient of the uranyl nitrate–tributylphosphate complex can be estimated fairly accurately by use of Einstein–Stokes relation. It can be seen from Table IV that the product of D and η is nearly constant whereas the viscosity varies by 300%. Probably, as a consequence of evaporation, there is a deviation of 10% for the results in the mixtures of TBP and hexane and therefore in these systems the higher values must be doubted. The higher values obtained in TBP and 90/10 TBP/C_{12} indicate that, in the pure solvent system, the interactions between solvent and complex cannot be completely neglected. In order to elucidate the validity of using Stokes equation and to give firmer conclusions, studies of the diffusion of small molecules in various solvents with the aid of the analytical ultracentrifuge will be continued.

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