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Density, Viscosity, and Electric Conductance of a Ternary Solution of (Nicotinic Acid + Dextran 40000 + Water)

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Supporting Information

ABSTRACT: In this work, the density, viscosity, and electrical conductance of a ternary solution of {water + dextran + nicotinic acid} were determined experimentally. The data of electric conductance show that the dissociation of nicotinic acid is little influenced by the addition of dextran. The data of density indicate that with the addition of dextran a maximum of the solvation volume of nicotinic acid is observed. The *B*-coefficient of viscous flow was evaluated from viscosity data. Using Eyring's transition state treatment, the activation parameters of viscous flow, which reflect the effect of the concentration of dextran on the motion of nicotinic acid, have been obtained. The result shows that dextran impedes the movement of the molecular nicotinic acid.

INTRODUCTION

Many drugs are hydrophobic organic compounds and show a rather lower solubility and dissolution rate in water. These properties lower their medicine efficiency and bioavailability. To improve the dissolution rate, there are two things to be done. One is to enhance their solubility in water. Another is to improve their diffusivity. Some effective techniques improving solubility have been developed in pharmaceutical processes: one of them is to introduce some polymer additives into the drug carrier to form solid dispersion.[1−3] Polymers such as poly(ethylene glycol) (PEG), poly(vinylpyrrolidone) (PVP), and Dextran are commonly used in pharmaceutical techniques to improve the stability and bioavailability of drugs.[4−6]

A drug additive can improve the drug solubility but often causes the increase in the viscosity of the medium and therefore limits the diffusion of drug. This contradicting role played by the drug carrier and additives has been our interest in recent years.[7−9]

Drug diffusion rate in aqueous solution is basically governed by the restrictive effect of the additive on drug mobility, whether due to a reduction in free volume or an increase in medium viscosity. Systems of this type generally show an inverse relationship between diffusion rate and viscosity, which is predicted by the Stokes−Einstein equation. This has led to viscosity being used as a predictor of resistance against diffusion.

Some drugs are hydrophobic organic weak acids or bases. Their solubility is determined partly by their dissociation constant.[10] Generally, the solubility of a poorly soluble weak acid/base will be improved greatly by the process of ionization.[11] For drug solid dispersions, our interest is whether the addition of polymer will influence the ionization equilibrium of acid or base and so influence their diffusion? The answer is different for different (drug + polymer) systems because it is determined by the drug structure and the solute−solvent interaction.

In our previous work, we have studied the effect of some polymers on the solubility of some drugs of flavonolignans.[7,12] We have also studied the effect of some polymers on the diffusion of some poorly soluble weak acid with linear structure in aqueous solution by viscosity.[8] In this work, we turn our attention to the diffusion of some drugs with simple cyclic structure. Therefore, nicotinic acid dissolved in aqueous dextran solution is selected as a model system for consideration.

In this work, the density, viscosity, and electrical conductance of a ternary solution of (nicotinic acid + dextran 40000 + water) were measured. The dissociation behavior of nicotinic acid in aqueous dextran solution was studied through electric conductivity, the solute hydration through density, and the diffusion behavior through viscosity. Using Eyring's transition state treatment, the activation parameters of viscous flow, which reflects the effect of the concentration of dextran on the motion of nicotinic acid, can be obtained.

EXPERIMENTAL SECTION

Materials. Dextran 40000 (mass average molar mass is 33.8 $\text{kg}\cdot\text{mol}^{-1}$ determined by the intrinsic viscosity method) was supplied by the Shanghai Chemical Reagent Inc. and used in experiments without further purification. Nicotinic acid, mass fraction > 0.995, was supplied by the Shanghai Chemical Reagent Inc. and dried under vacuum at 323 K for 5 h before use. Water was purified by distilling the deionized water from alkaline $KMnO_4$ solution to remove organic matter and was degassed under vacuum to evaporate the air before use.

Density Measurement. Dextran aqueous solutions with given concentrations were prepared. Its concentration is controlled in a dilute range to prevent the formation of a molecular cluster. Nicotinic acid was dissolved in aqueous dextran solution to form ternary solution. Densities were measured with an Anton Paar DMA 602 vibrating tube densimeter with an uncertainty of $\pm$ 0.00005 $\text{g}\cdot\text{cm}^{-3}$. The temperature of the cell was controlled by circulating water from a water bath with the temperature within

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Table 1. Density ρ for {Water (1) + Dextran (2) + Nicotinic Acid (3)} from T = (293.15 to 313.15) K as a Function of Molality m_3

m_3	ρ/g·cm^{-3}				
mol·kg^{-1}	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
			c_2/g·dm^{-3} = 0		
0	0.99820	0.99704	0.99564	0.99404	0.99222
0.004283	0.99841	0.99722	0.99582	0.99428	0.99241
0.006512	0.99850	0.99730	0.99595	0.99435	0.99259
0.008190	0.99857	0.99741	0.99601	0.99440	0.99264
0.01628	0.99883	0.99773	0.99631	0.99475	0.99298
0.03262	0.99956	0.99836	0.99697	0.99544	0.99351
0.04903	1.00025	0.99909	0.99772	0.99614	0.99422
0.06555	1.00089	0.99971	0.99832	0.99672	0.99491
0.08210	1.00166	1.00045	0.99903	0.99741	0.99556
0.09871	1.00229	1.00109	0.99967	0.99805	0.99621
0.1154	1.00305	1.00180	1.00033	0.99871	0.99684
0.1321	1.00375	1.00251	1.00103	0.99939	0.99749
			c_2/g·dm^{-3} = 1.6206		
0	0.99875	0.9976	0.99619	0.99455	0.99272
0.008169	0.99913	0.99799	0.99654	0.99495	0.99310
0.02039	0.99960	0.99846	0.99703	0.99540	0.99354
0.03264	1.00009	0.99893	0.99748	0.99585	0.99399
0.04506	1.00054	0.99944	0.99793	0.99633	0.99445
0.05741	1.00112	0.99990	0.99844	0.99681	0.99497
0.06981	1.00161	1.00045	0.99899	0.99732	0.99545
0.08208	1.00211	1.0009	0.99943	0.99776	0.99587
0.09457	1.00266	1.00147	0.99997	0.99829	0.99639
			c_2/g·dm^{-3} = 3.2412		
0	0.99925	0.99809	0.99664	0.99505	0.99323
0.008174	0.99972	0.99856	0.99714	0.99554	0.99367
0.02043	1.00025	0.99910	0.99768	0.99604	0.99418
0.03269	1.00074	0.99957	0.99816	0.99646	0.99474
0.04492	1.00119	1.00003	0.99856	0.99691	0.99504
0.05725	1.00159	1.00043	0.99897	0.99731	0.99544
0.06980	1.00221	1.00104	0.99958	0.99791	0.99603
0.08212	1.00269	1.00150	1.00004	0.99837	0.99648
0.09470	1.00319	1.00197	1.00051	0.99883	0.99697
			c_2/g·dm^{-3} = 4.8615		
0	1.00001	0.99887	0.99747	0.99587	0.99403
0.008169	1.00032	0.99915	0.99773	0.99611	0.99427
0.02037	1.00083	0.99966	0.99821	0.99658	0.99477
0.03270	1.00136	1.00019	0.99876	0.99713	0.99531
0.04504	1.00188	1.00070	0.99928	0.99764	0.99580
0.05725	1.00232	1.00115	0.99970	0.99808	0.99622
0.06952	1.00288	1.00169	1.00023	0.99860	0.99675
0.08196	1.00346	1.00227	1.00082	0.99916	0.99729
0.09483	1.00396	1.00276	1.00129	0.99964	0.99777
			c_2/g·dm^{-3} = 8.1026		
0	1.00097	0.99978	0.99839	0.99674	0.99500
0.008142	1.00132	1.00019	0.99876	0.99713	0.99536
0.02034	1.00197	1.00078	0.99937	0.99776	0.99592
0.03253	1.00249	1.00116	0.99991	0.99829	0.99648
0.04500	1.00307	1.00188	1.00045	0.99884	0.99699
0.05717	1.00346	1.00226	1.00081	0.99918	0.99741

Table 1. Continued

m_3	$\rho/g\cdot cm^{-3}$				
$mol\cdot kg^{-1}$	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0.06969	1.00408	1.00287	1.00147	0.99981	0.99797
0.08197	1.00458	1.00336	1.00193	1.00029	0.99847
0.09410	1.00511	1.00388	1.00247	1.0008	0.99900
			$c_2/g\cdot dm^{-3}$ = 11.3437		
0	1.00220	1.00107	0.99967	0.99805	0.99626
0.008158	1.00255	1.00139	0.99999	0.99837	0.99655
0.02036	1.00301	1.00188	1.00042	0.99883	0.99700
0.03260	1.00378	1.00257	1.00116	0.99953	0.99771
0.04503	1.00418	1.00298	1.00156	0.99993	0.99811
0.05739	1.00481	1.00359	1.00216	1.00050	0.99868
0.06975	1.00527	1.00407	1.00263	1.00099	0.99916
0.08227	1.00588	1.00470	1.00322	1.00159	0.99973
0.09459	1.00642	1.00519	1.00376	1.00209	1.00027

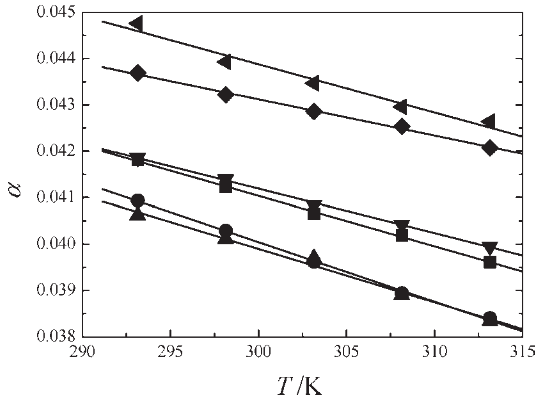

Figure 1. Linear relationship between α and temperature T for solution with constant $c_2/g\cdot dm^{-3}$: ■, 0; ●, 1.6206; ▲, 3.2412; ▼, 4.8615; ♦, 8.1026; solid triangle pointing left, 11.3437.

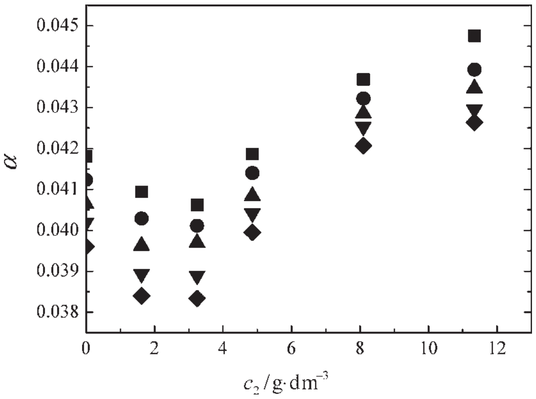

Figure 2. Effect of c_2 on the density linear coefficient α at T: ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ▼, 308.15 K; and ♦, 313.15 K.

Table 2. Linear Coefficients of α_0 and α_1 in Equation 1 for Solutions with Concentrations of c_2[a]

c_2	α_0	$10^4\cdot\alpha_1$		
$g\cdot dm^{-3}$	$(g\cdot cm^{-3}/mol\cdot kg^{-1})$	$(g\cdot cm^{-3}/mol\cdot kg^{-1}\cdot K^{-1})$	R	$10^5\cdot s$
0	0.0737	−1.09	0.9993	3.7
1.6206	0.0786	−1.29	0.9993	4.4
3.2412	0.0745	−1.15	0.9945	1.1
4.8615	0.0700	−0.96	0.9992	3.6
8.1026	0.0666	−0.78	0.9977	4.8
11.3437	0.0751	−1.04	0.9862	1.5

[a] R is the correlation coefficient, and s is the standard deviation of the Fit.

± 0.01 K. The densimeter was calibrated by using the purified water as a calibration substance.

Viscosity Measurement. The kinematic viscosity (ν) was measured by means of suspended level Ubbelohde viscometer. The efflux time of fluid was measured with a digital stopwatch to ± 0.1 s. The viscometer was kept in a water thermostat controlled to ± 0.01 K. The kinematic viscosity (ν) and the dynamic viscosity (η) are given by following equations: $\nu = Lt - K/t$ and $\eta = \nu\rho$, where t is the efflux time of fluid; ρ is the density of solution; and L and K are the characteristic constants of a viscometer. The values of L and K were determined from a calibration process, which was performed in following steps: measuring the efflux time of the twice distilled water in a viscometer from temperatures (288.15 to 318.15) K at an interval of 5 K, respectively, using the values of ρ and η from the literature[13] and by the least-squares method to fit the experimental efflux time, and then the values of L and K were obtained. Two viscometers were used in experiments. The value of L and K for each viscometer is, for example: viscometer (1), $L = 0.007294$, $K = 25.98$; and viscometer (2), $L = 0.007146$, $K = 23.96$ (η, mPa·s; t, s; ρ, $g\cdot cm^{-3}$). In the process of viscosity determination, for every sample at given temperature, efflux time was measured by two viscometers at the same time, respectively. For each viscometer, determination was performed at least in 10 replicates. The results obtained by two viscometers were averaged. Then η was calculated from t and ρ, and the estimated relative standard deviation for η was ± 0.1 %.

Electrical Conductivity Measurement. Electrical conductivity was measured using a digital conductivity meter, CON 1500 model, EUTECH Company, with a cell having platinum electrodes. The electrode was calibrated by a standard sample of KCl aqueous solution at different temperatures to obtain the cell constant. The literature value of conductivity of KCl aqueous

Table 3. Partial Molar Volume $V_3{}^0$ of Nicotinic Acid in Aqueous Dextran Solution at Infinite Dilution

c_2	$V_3{}^0/\mathrm{cm^3 \cdot mol^{-1}}$				
$\mathrm{g \cdot dm^{-3}}$	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0	81.37	82.00	82.64	83.17	83.84
1.6206	82.22	82.92	83.65	84.41	85.05
3.2412	82.51	83.07	83.55	84.43	85.08
4.8615	81.25	81.76	82.37	82.86	83.42
8.1026	79.38	79.90	80.31	80.69	81.23
11.3437	78.27	79.14	79.65	80.22	80.61

solution was obtained from the literature.[14] The cell constant is 1.024 $\mathrm{cm^{-1}}$. According to the instruction of the instrument manual, the optimal conductivity range for this electrode is from (10 to 2000) $\mu\mathrm{S \cdot cm^{-1}}$.

The conductivity was measured in a glass container, where the sample solution was stirred by an electromagnetic stirrer. The temperature of the container was controlled by a water bath with a precision of ± 0.01 K. The container was sealed with a rubber cap, through which the conductivity cell had been inserted. Conductivity was determined in the following procedure. A weighted amount of water was transferred to the container. After the temperature was held at the desired value for 10 min, conductivity data were read at least three times. Then a gastight syringe with 0.5 mL capacity was used to inject 0.1 mL of nicotinic acid solution (with known concentration) into the container. The concentration of the new solution was calculated from the amount of mixing. After 10 min equilibrium, new conductivity data were recorded. Then another injection and recording followed. In this way, the conductivities of solution with different concentration were recorded. The relative error of the measurements is < 0.1 %.

RESULTS AND DISCUSSION

Density. Densities of the ternary solution of {water (1) + dextran (2) + nicotinic acid (3)} are listed in Table 1. Ternary solutions were prepared by dissolving nicotinic acid in aqueous dextran solutions with several constant concentrations $c_2/\mathrm{g \cdot dm^{-3}}$. The concentration of nicotinic acid (m_3) is less than 0.2 $\mathrm{mol \cdot kg^{-1}}$, which is in a dilute concentration range. Generally, for solid dissolved in liquid, the relation between the density and the concentration of a solute can be expressed by a polynomial equation. However, for ternary solutions with a constant c_2 and m_3 varying in the dilute concentration range at constant temperature T, our experimental result shows that the linear relationship between density and the concentration of m_3 agrees well with experimental data.

$$\rho_{123} = \rho_{12} + \alpha m_3 = \rho_{12} + (\alpha_0 + \alpha_1 T)m_3 \qquad (1)$$

where $m_3/\mathrm{mol \cdot kg^{-1}}$ is the molality of nicotinic acid in dextran aqueous solution and ρ_{123} and ρ_{12} represent the density of the solution (1 + 2 + 3) and (1 + 2), respectively. The parameter α is a linear coefficient for solutions with a given concentration c_2 and temperature T, which is obtained by a least-squares regression method. The effect of T on α at constant c_2 is shown in Figure 1, which can be expressed by a linear relationship, $\alpha = \alpha_0 + \alpha_1 T$, as shown in the second part of eq 1. The parameters α_0 and α_1 were obtained by fitting α against T, and their values are provided in Table 2. The effect of c_2 on α at constant T is shown in Figure 2, where a minimum is observed around the concentration about 3 $\mathrm{g \cdot dm^{-3}}$.

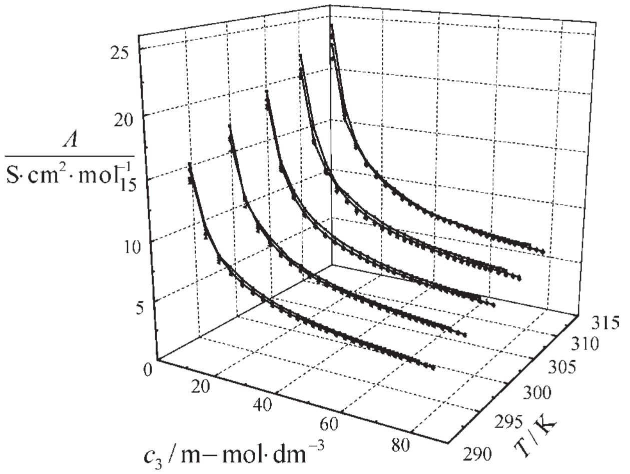

Figure 3. 3D-curves of $\Lambda - T - c_3$ for solutions of {water (1) + dextran (2) + nicotinic acid (3)} with concentration of c_2 = (0, 1.6206, 3.2412, 4.8615, 8.1026, and 11.3437) $\mathrm{g \cdot dm^{-3}}$. However, at constant temperature T, we cannot see the separate curves of Λ vs c_3 for every solution with different c_2 because they overlap and become nearly one line.

The partial molar volume of a solute 3 at infinite dilution, $V_3{}^0$, can be calculated from α by eq 2.[15]

$$V_3{}^0 = \frac{M_3}{\rho_{12}} - \frac{1000\alpha}{\rho_{12}^2} \qquad (2)$$

where M_3 is the mole mass of component 3. The value of $V_3{}^0$ is shown in Table 3. This equation indicates that the minimum of the coefficient of α against c_2 in Figure 2 corresponds to a maximum of $V_3{}^0$. The partial molar volume of a solute at infinite dilution may be expressed as[16−18]

$$V_3{}^0 = V_M + V_V + V_I + \beta RT \qquad (3)$$

where V_M is the intrinsic molar volume of a solute. V_V describes the thermal volume that is a volume resulting from mutual thermal motions of solute and solvent molecules. The term V_I specifies the so-called interaction volume which reflects the interaction between the solute and solvent. The term of βRT is the ideal component of the partial molar volume resulting from the motion of the molecule along the translational degrees of freedom and is often neglected for aqueous solution. Therefore, the phenomenon that the minimum of α in Figure 2 corresponds to the maximum of $V_3{}^0$ is due to the change in the term of $V_V + V_I$, which reflects the change in the

Table 4. Viscosity η for {Water (1) + Dextran (2) + Nicotinic Acid (3)} from T = (293.15 to 313.15) K as a Function of Molality m_3

m_3	$\eta/\text{mPa}\cdot\text{s}$				
$\text{mol}\cdot\text{kg}^{-1}$	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
			$c_2/\text{g}\cdot\text{dm}^{-3} = 0$		
0	1.003	0.890	0.797	0.719	0.653
0.004283	1.004	0.891	0.798	0.720	0.654
0.006512	1.005	0.892	0.799	0.721	0.654
0.008188	1.006	0.892	0.799	0.721	0.655
0.01628	1.007	0.894	0.801	0.722	0.656
0.03262	1.011	0.898	0.804	0.725	0.659
0.04903	1.015	0.901	0.807	0.728	0.661
0.06555	1.018	0.904	0.810	0.731	0.664
0.08210	1.022	0.907	0.813	0.734	0.666
0.09871	1.026	0.911	0.816	0.736	0.669
0.1154	1.029	0.914	0.819	0.740	0.671
0.1321	1.033	0.918	0.823	0.742	0.674
			$c_2/\text{g}\cdot\text{dm}^{-3} = 1.6206$		
0	1.028	0.913	0.817	0.738	0.670
0.008158	1.031	0.916	0.819	0.740	0.672
0.02448	1.035	0.919	0.823	0.743	0.674
0.04097	1.039	0.922	0.827	0.746	0.677
0.05729	1.043	0.926	0.829	0.748	0.680
0.07396	1.047	0.930	0.833	0.751	0.683
0.09045	1.051	0.934	0.837	0.755	0.685
0.1070	1.056	0.938	0.839	0.758	0.689
0.1236	1.061	0.942	0.844	0.762	0.692
			$c_2/\text{g}\cdot\text{dm}^{-3} = 3.2412$		
0	1.056	0.937	0.838	0.756	0.686
0.008167	1.058	0.939	0.841	0.760	0.688
0.03274	1.065	0.944	0.846	0.763	0.692
0.05743	1.073	0.951	0.851	0.769	0.698
0.08209	1.078	0.958	0.857	0.773	0.702
0.1068	1.085	0.963	0.863	0.778	0.707
0.1321	1.094	0.970	0.869	0.784	0.712
			$c_2/\text{g}\cdot\text{dm}^{-3} = 4.8615$		
0	1.085	0.962	0.860	0.774	0.702
0.008169	1.089	0.964	0.861	0.776	0.704
0.02037	1.091	0.967	0.865	0.779	0.707
0.03270	1.096	0.971	0.868	0.782	0.710
0.04504	1.100	0.974	0.872	0.785	0.713
0.05725	1.102	0.978	0.875	0.788	0.716
0.06952	1.107	0.981	0.879	0.791	0.718
0.08196	1.110	0.984	0.881	0.793	0.720
0.09483	1.114	0.988	0.883	0.797	0.721
			$c_2/\text{g}\cdot\text{dm}^{-3} = 8.1026$		
0	1.140	1.010	0.902	0.813	0.735
0.008142	1.143	1.013	0.905	0.816	0.738
0.02034	1.148	1.017	0.909	0.819	0.741
0.03253	1.154	1.021	0.912	0.823	0.744
0.04500	1.159	1.026	0.917	0.826	0.748
0.05717	1.161	1.029	0.920	0.830	0.751
0.06969	1.166	1.033	0.924	0.833	0.754
0.08197	1.171	1.038	0.927	0.837	0.757

Table 4. Continued

m_3	η/mPa·s				
mol·kg^{-1}	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0.09410	1.177	1.043	0.932	0.840	0.761
		c_2/g·dm^{-3} = 11.3437			
0	1.199	1.063	0.948	0.853	0.773
0.008158	1.204	1.066	0.951	0.857	0.776
0.02036	1.208	1.071	0.955	0.861	0.779
0.03260	1.216	1.076	0.961	0.865	0.784
0.04503	1.221	1.081	0.965	0.869	0.787
0.05739	1.228	1.086	0.970	0.874	0.791
0.06975	1.233	1.092	0.975	0.878	0.795
0.08227	1.239	1.097	0.980	0.882	0.800
0.09459	1.243	1.102	0.984	0.887	0.803

interaction between solute and solvent as the concentration of dextran changes. The increase in $V_V + V_I$ means the volume of the solvation shell is increased.

Electrical Conductance and the Degree of Dissociation. For the system of nicotinic acid (3) solved in solutions of {water (1) + dextran (2)} with several constant concentrations of c_2 = (0, 1.6206, 3.2412, 4.8615, 8.1026, and 11.3437) g·dm^{-3}, the electric conductivity (κ) was measured by a conductivity meter at T = (293.15, 298.15, 303.15, 308.15, and 313.15) K. Taking into account the influence of solvents on the conductivity, the molar conductance of nicotinic acid (Λ) is calculated by

$$\Lambda = \frac{\kappa - \kappa_0}{c_3} \qquad (4)$$

where,κ_0 is the conductivity of solvent (water + dextran). The data of Λ of nicotinic acid in (water + dextran) solvents is provided in the tables in the Supporting Information. For convenience, to see the relationship between Λ and the concentration of c_3, corresponding figures are attached after each table. To see the influence of c_2 on Λ, the 3-D curves of $\Lambda - T - c_3$ for every solution with constant c_2 are plotted in Figure 3. However, it shows that the curves of Λ against c_3 at constant T are not separate lines for solutions with different c_2, as they overlap and become nearly one line. It means that the influence of c_2 on the curve of $\Lambda - c_3$ at constant T is much smaller and that the effect of dextran on the dissociation of nicotinic acid is not observable.

To estimate the degree of dissociation (β), the limiting molar conductance of nicotinic acid in dextran + water solvent (Λ^∞) is supposed to be the same as they are in water, which can be obtained from the literature.[19] The degree of dissociation β of nicotinic acid is calculated by eq 5.

$$\beta = \Lambda/\Lambda^\infty \qquad (5)$$

In the experimental concentration region, β is very small. The value of β is useful in the analysis of viscosity.

Viscosity and the *B*-Coefficients of Viscous Flow. Viscosities of the ternary solution of {water (1) + dextran (2) + nicotinic acid (3)} are provided in Table 4. There, m_3 can be converted to c_3 by using density data. For a weak electrolyte solution with a degree of dissociation β in the dilute concentration region, the Jones-Dole equation was used to correlate viscosity and the concentration of weak electrolyte, c_3.

Table 5. Limiting Molar Conductance of Nicotinic Acid Λ^0 and the Ions λ^0 (H$^+$) and λ^0 (Nic$^-$) and the Dielectric Coefficient of Aqueous Solution ε[19]

T	Λ^0	λ^0 (H$^+$)	λ^0 (Nic$^-$)	
K	S·cm^2·mol^{-1}	S·cm^2·mol^{-1}	S·cm^2·mol^{-1}	ε
293.15	356.4	325.5	30.87	80.176
298.15	384.5	349.9	34.61	78.358
303.15	412.1	373.7	38.47	76.581
308.15	439.4	396.9	42.57	74.846
313.15	466.5	419.2	47.34	73.151

$$\eta_r = 1 + A(\beta c_3)^{1/2} + B(1-\beta)c_3 \qquad (6)$$

where η_r is the relative viscosity. The A-coefficient, which depends on the interionic force, can be evaluated theoretically by the Falkenhagen equation as described in some articles.[20]

$$A = \frac{0.2577\Lambda^0}{\eta_0(\varepsilon T)^{1/2}\lambda_+^0\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2\right] \qquad (7)$$

where A is in (dm^3·mol^{-1})$^{1/2}$. The molar conductance of ions at infinite dilution, λ_j^0/(S·cm^2·mol^{-1}), and the dielectric coefficient ε of solvent can be obtained from the literature,[19] which are listed in Table 5. The η_0/(Pa·s) is the viscosity of solvent. Using eq 6 to fit viscosity, the B-coefficient can be obtained with a standard error less than 0.003 dm^3·mol^{-1}. Because c_3 is located in the region where β is very small, only the contribution of an acid molecule to the B-coefficient was considered. Table 6 gives the values of A- and B-coefficients. The B-coefficient increases with both c_2 and T increase.

Activation Parameters of Viscous Flow. Applying Eyring's transition state treatment, the activation thermodynamic parameters of viscous flow are evaluated from viscosity. For pure solvent, Eyring's equation is

$$\eta_1 = (hN_A/V_{m1})\exp(\Delta\mu_1^{\ddagger 0}/RT) \qquad (8)$$

where N_A is Avogadro's number; h is Planck's constant; V_{m1} is the molar volume of solvent 1; and $\Delta\mu_1^{\ddagger 0}$ is the activation free energy of viscous flow of pure solvent 1.

Table 6. *A*- and *B*-Coefficients of the Viscous Flow of {Water (1) + Dextran (2) + Nicotinic Acid (3)}

c_2/g·dm^{-3}	*T*/K = 293.15	*T*/K = 298.15	*T*/K = 303.15	*T*/K = 308.15	*T*/K = 313.15
			$A/(\mathrm{dm^3 \cdot mol^{-1}})^{1/2}$		
0	0.0316	0.0324	0.0332	0.0340	0.0346
1.6206	0.0308	0.0316	0.0324	0.0331	0.0337
3.2412	0.0300	0.0308	0.0316	0.0323	0.0329
4.8615	0.0292	0.0300	0.0308	0.0316	0.0322
8.1026	0.0278	0.0286	0.0294	0.0301	0.0307
11.3437	0.0264	0.0271	0.0279	0.0286	0.0292
			$B/(\mathrm{dm^3 \cdot mol^{-1}})$		
0	0.223	0.228	0.232	0.236	0.241
1.6206	0.246	0.250	0.255	0.256	0.261
3.2412	0.260	0.263	0.269	0.272	0.282
4.8615	0.275	0.284	0.294	0.304	0.310
8.1026	0.330	0.338	0.346	0.358	0.363
11.3437	0.392	0.403	0.407	0.414	0.416

Table 7. Activation Parameters of Viscous Flow

c_2/g·dm^{-3}		*T*/K = 293.15	*T*/K = 298.15	*T*/K = 303.15	*T*/K = 308.15	*T*/K = 313.15
	$\Delta H_{m12}^\ddagger$/kJ·mol^{-1}	$\Delta\mu_{12}^\ddagger$/kJ·mol^{-1}				
0	16.1	9.30	9.16	9.04	8.93	8.83
1.6206	16.1	9.36	9.23	9.11	9.00	8.90
3.2412	16.2	9.43	9.29	9.17	9.06	8.96
4.8615	16.3	9.49	9.36	9.24	9.13	9.02
8.1026	16.5	9.62	9.49	9.36	9.26	9.15
11.3437	16.5	9.74	9.62	9.49	9.39	9.29
	$\Delta H_{m3}^\ddagger$/kJ·mol^{-1}	$\Delta\mu_3^\ddagger$/kJ·mol^{-1}				
0	−20.9	48.0	49.3	50.4	51.5	52.8
1.6206	−15.4	51.2	52.4	53.7	54.5	55.8
3.2412	−29.9	53.1	54.3	55.7	56.8	58.9
4.8615	−60.5	55.0	56.9	59.0	61.1	62.8
8.1026	−54.5	62.2	64.1	65.9	68.4	70.0
11.3437	−31.7	70.5	72.9	74.4	76.2	77.5

For a binary solution of solute 2 solves in solvent 1, Eyring's equation is written as

$$\eta_{12} = (hN_A/V_{m12})\exp(\Delta\mu_{12}^\ddagger/RT) \qquad (9)$$

where V_{m12} is the mean molar volume of the solution $(1 + 2)$ and $\Delta\mu_{12}^\ddagger$ is the average free energy of activation for the viscous flow of $(1 + 2)$. Because V_{m12} and η_{12} are measurable variables, $\Delta\mu_{12}^\ddagger$ can be calculated from eq 9.

For the ternary system in this work, we can split the free energy $\Delta\mu_{123}^\ddagger$ into two parts.

$$\Delta\mu_{123}^\ddagger = x_{12}\Delta\mu_{12}^\ddagger + x_3\Delta\mu_3^\ddagger \qquad (10)$$

where $\Delta\mu_3^\ddagger$ and $\Delta\mu_{12}^\ddagger$ represent the contribution from solute 3 and solvent $(1 + 2)$, respectively. On the basis of the method of Feakins et al.,[21,22] an equation correlating the *B*-coefficient with the activation free energy is given by eq 11.

$$B = (\nu V_{m12} - V_3{}^0) + (V_{m12}/RT)(\Delta\mu_3^\ddagger - \nu\Delta\mu_{12}^\ddagger) \qquad (11)$$

where $V_3{}^0$ is the partial molar volume of solute 3 at infinite dilution; V_{m12} is the mean mole volume of mixed solvent $(1 + 2)$; and ν is one for nonelectrolyte. Once the *B*-coefficient is determined from eq 6, the value of $\Delta\mu_3^\ddagger$ can be calculated from eq 11.

If $\Delta\mu_3^\ddagger$ were known at some temperatures, the mole activation enthalpy of solute 3 can be calculated by

$$d(\Delta\mu_3^\ddagger/T)/d(1/T)_p = \Delta H_{m3}^\ddagger \qquad (12)$$

The mole activation entropy of solute 3 can be calculated by eq 13.

$$\Delta S_{m3}^\ddagger = (\Delta H_{m3}^\ddagger - \Delta\mu_3^\ddagger)/T \qquad (13)$$

In this work, the $\Delta\mu_{12}^\ddagger$ of a binary solution of {water (1) + dextran (2)} was calculated from their viscosity η_{12}. The V_{m12} is calculated from their density. The segment mass of dextran is $M_2 = 162.053$. For the convenience of calculation, segment mass was used to substitute the molecular mass to calculate the concentration. From the linear slope of $\Delta\mu_{12}^\ddagger/T$ against $1/T$, the viscous activation enthalpy, $\Delta H_{m,12}^\ddagger$, was obtained. In Table 7, some activation thermodynamic properties of viscous flow of dextran aqueous solution are listed.

For ternary solution, $\Delta\mu_3^\ddagger$ was calculated by eq 11. The activation enthalpy, $\Delta H_{m,3}^\ddagger$, was calculated from the linear slope of $(\Delta\mu_3^\ddagger/T)$ against $(1/T)$, which is shown in Figure 4. The activation

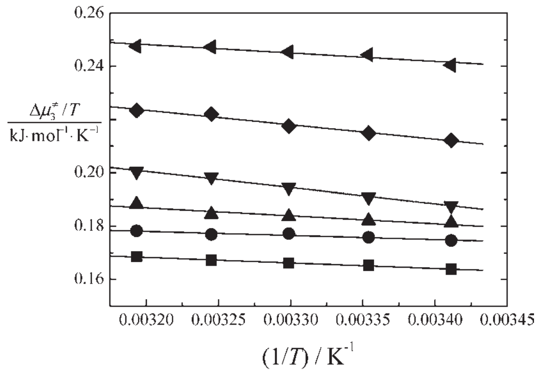

Figure 4. $\Delta\mu_3^{\ddagger}/T$ against $1/T$ and the linear fit for nicotinic acid in dextran aqueous solution with c_2/g·dm^{-3}: ■, 0; ●, 1.6206; ▲, 3.2412; ▼, 4.8615; ♦, 8.1026; solid triangle pointing left, 11.3437.

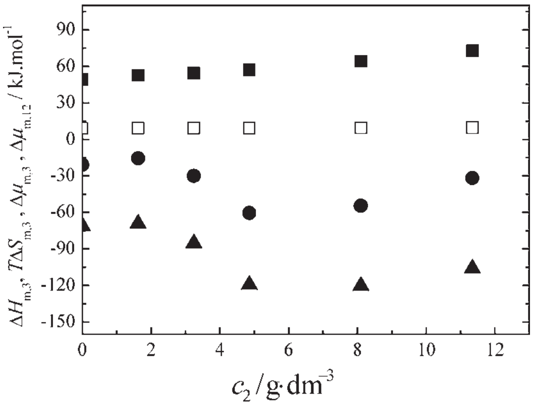

Figure 5. Effect of the concentration of dextran on the activation parameters of ■, $\Delta\mu_{\mathrm{m},3}^{\ddagger}$/kJ·mol^{-1}; ●, $\Delta H_{\mathrm{m},3}^{\ddagger}$/kJ·mol^{-1}; ▲, $T\Delta S_{\mathrm{m},3}^{\ddagger}$/kJ·mol^{-1}; and □, $\Delta\mu_{\mathrm{m},12}^{\ddagger}$/kJ·mol^{-1} at 298.15 K.

entropy was calculated by eq 13. The activation parameters are listed in Table 7. The standard error of the B-coefficient is $<$ 0.003 dm^3·mol^{-1}. According to eq 11, the error of $\Delta\mu_3^{\ddagger}$ is estimated to be 0.4 kJ·mol^{-1}. For the linear fit in Figure 4, the standard error is less than 0.0004.

The effect of c_2 on activation parameters $\Delta\mu_{\mathrm{m},12}^{\ddagger}$, $\Delta\mu_3^{\ddagger}$, $\Delta H_{\mathrm{m},3}^{\ddagger}$, and $T\Delta S_{\mathrm{m},3}^{\ddagger}$ at 298.15 K is shown in Figure 5. It shows that $\Delta\mu_{\mathrm{m},12}^{\ddagger}$ changes little with c_2. $\Delta\mu_3^{\ddagger}$ values are positive and increase with c_2. However, $\Delta H_{\mathrm{m},3}^{\ddagger}$ and $T\Delta S_{\mathrm{m},3}^{\ddagger}$ are negative, and their curves rise and fall with c_2 increase.

■ CONCLUSION

Electric conductance data show that the dissociation of nicotinic acid is little influenced by the addition of dextran. Density data indicate that, with the addition of dextran, a minimum value of the α coefficient, which corresponds to a maximum of the solvation volume of nicotinic acid, is observed at about 3 g·dm^{-3} of dextran. Viscosity data reveal that $\Delta\mu_3^{\ddagger}$ is positive and increases with the concentration of dextran, which impedes the movement of the molecular acid.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** The experimental data of the molar electric conductance are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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