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

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In this work, the density, viscosity, and electrical conductance of the ternary solution of {nicotinic acid + polyethanol + water} were determined experimentally; polyethanol is commonly known as poly(vinyl alcohol) given the acronym PVA. The degree of dissociation, the partial molar volume of nicotinic acid in PVA aqueous solution, and the *B*-coefficient of viscous flow were evaluated. The effect of PVA on these parameters was discussed. Using Eyring's transition state treatment, the activation parameters of viscous flow, which reflects the effect of the concentration of PVA on the motion of nicotinic acid, have been obtained. The result shows that PVA increases the viscosity, decreases the degree of dissociation, and impedes the motion of nicotinic acid at lower concentrations but promotes the solubility and molecular diffusion of nicotinic acid at higher concentrations.

Introduction

Some effective components of drugs are weak organic electrolytes. The degree of dissociation is determined mainly by the medium. In pharmaceutical techniques, materials of pharmaceutical aids are usually introduced to enhance the bioavailability of drugs. The effect of the composition of carrier on the dissolution and diffusion of drugs has been our interest in recent years.[1,2]

Polyethanol (poly(vinyl alcohol), PVA) is commonly used as a component to form hydrogels. PVA hydrogels have been used in a number of biomedical applications and drug delivery matrices.[3,4] This is because of their inherent nontoxicity and good biocompatibility as well as their rubbery and swelling nature in aqueous solutions. The drug release rate in the hydrogel system is basically governed by the restrictive effect of the polymer on drug mobility due to either a reduction in free volume or an increase in medium viscosity. This process generally shows an inverse relationship between release rate and viscosity, which is predicted by the Stokes−Einstein equation, so that medium viscosity has been used as a routine predictor of resistance to diffusion.[5,6]

In this work, nicotinic acid was selected as a model molecule of weak organic electrolyte drug. The experimental density, viscosity, and electrical conductance of the ternary solution of (nicotinic acid + PVA + water) were reported. The degree of dissociation, the equilibrium constant of dissociation, the partial molar volume of nicotinic acid in PVA aqueous solution, and the *B*-coefficient of viscous flow were evaluated. The effect of PVA on these parameters was discussed. Using Eyring's transition state treatment, the activation parameters of viscous flow, which reflects the effect of the concentration of PVA on the motion of nicotinic acid, have been obtained.

Experimental Section

Materials. PVA (mass fraction > 0.99; mass average molar mass is 68.8 kg·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 solved in before use.

Density Measurement. PVA aqueous solutions with given concentrations were prepared. The concentration of PVA is controlled in a dilute range to interrupt the formation of hydrogel. Nicotinic acid was dissolved in PVA aqueous solutions to form the ternary solution. Densities were measured with an Anton Paar DMA 602 vibrating tube densimeter with an uncertainty of ± 0.00005 g·cm^{-3}. The temperature of the cell was controlled by circulating water from a water bath with the temperature within ± 0.01 K. The densimeter was calibrated by using the purified water and dry air as calibration substances.

Viscosity Measurement. Viscosities were measured by a suspended level Ubbelohde viscometer. The efflux time of the fluid was measured with a digital stopwatch to ± 0.01 s. The viscometer was kept in a water thermostat controlled to ± 0.01 K. Viscometers were calibrated by the purified water as described in our previous work.[5] Two viscometers were used in experiment. Detection was performed at least in six replicates for each composition at each temperature. The estimated relative standard deviation for η was ± 0.1 %. The reference data for density and viscosity calibration are from literature.[7] Other experimental details and procedures are the same as those described in our previous work.[5]

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.[8] The cell constant is 1.024 cm^{-1}. According to the instructions of the instrument manual, the optimal conductivity range of this electrode is from (10 to 2000) μS·cm^{-1}.

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Table 1. Density, ρ/g·cm^{-3}, of a Ternary Solution of {Water (1) + PVA (2) + Nicotinic Acid (3)}

m_3	ρ/g·cm^{-3}				
mol·kg^{-1}	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
$c_2 = 0$ g·dm^{-3}					
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
0.00819	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
$c_2 = 0.5007$ g·dm^{-3}					
0	0.99829	0.99714	0.99573	0.99412	0.99235
0.004096	0.99845	0.99729	0.99591	0.99432	0.99255
0.008155	0.99862	0.99745	0.99609	0.99451	0.99271
0.01630	0.99897	0.99775	0.99639	0.99477	0.99305
0.03263	0.99975	0.99851	0.99714	0.99545	0.99371
0.04907	1.00038	0.99915	0.99778	0.99611	0.99434
0.06552	1.00107	0.99987	0.99844	0.99682	0.99498
0.08209	1.00171	1.00054	0.99909	0.99747	0.99556
0.09840	1.00239	1.00116	0.99979	0.99808	0.99628
0.1154	1.00307	1.00191	1.00049	0.99878	0.99695
0.1320	1.00378	1.00249	1.00102	0.99940	0.99761
$c_2 = 1.0006$ g·dm^{-3}					
0	0.99843	0.99726	0.99587	0.99433	0.99244
0.004112	0.99863	0.99753	0.99613	0.99455	0.99271
0.008180	0.99882	0.99767	0.99628	0.99473	0.99286
0.01625	0.99923	0.99801	0.99662	0.99503	0.99312
0.03267	0.99987	0.99868	0.99731	0.99573	0.99381
0.04906	1.00055	0.99940	0.99795	0.99640	0.99451
0.06540	1.00121	1.00008	0.99865	0.99703	0.99513
0.08203	1.00193	1.00067	0.99928	0.99765	0.99578
0.09870	1.00253	1.00135	0.99990	0.99832	0.99636
0.1154	1.00322	1.00205	1.0006	0.99898	0.99703
$c_2 = 2.0003$ g·dm^{-3}					
0	0.99867	0.99751	0.99608	0.994471	0.99266
0.004080	0.99881	0.99759	0.99618	0.99455	0.99278
0.008164	0.99900	0.99785	0.99642	0.99481	0.99301
0.01632	0.99929	0.99817	0.99677	0.99518	0.99331
0.03264	1.00001	0.99887	0.99741	0.99580	0.99403
0.04908	1.00068	0.99944	0.99805	0.99644	0.99459
0.06554	1.00130	1.00013	0.99868	0.99710	0.99522
0.08211	1.00203	1.00084	0.99943	0.99778	0.99593
0.09871	1.00270	1.00146	1.00008	0.99838	0.99655
0.1154	1.00340	1.00225	1.00070	0.99904	0.99718
$c_2 = 4.0006$ g·dm^{-3}					
0	0.99917	0.99799	0.99656	0.99493	0.99312
0.004072	0.99928	0.99809	0.99663	0.99502	0.99330
0.008164	0.99943	0.99828	0.99690	0.99531	0.99348
0.01624	0.99974	0.99854	0.99709	0.99559	0.99381
0.03256	1.00039	0.99920	0.99782	0.99617	0.99440
0.04908	1.00110	0.99991	0.99853	0.99692	0.99512
0.06553	1.00178	1.00056	0.99917	0.99754	0.99567
0.08208	1.00251	1.00132	0.99986	0.99824	0.99634
0.09867	1.00308	1.00191	1.00042	0.99877	0.99703
0.11536	1.00385	1.00264	1.00118	0.99951	0.99765
$c_2 = 6.0004$ g·dm^{-3}					
0	0.99968	0.99849	0.99704	0.99540	0.99358
0.004072	0.99978	0.99862	0.99722	0.99563	0.99382
0.008172	0.99995	0.99878	0.99741	0.99580	0.99402
0.01630	1.00025	0.99906	0.99771	0.99611	0.99429
0.03266	1.00089	0.99969	0.99832	0.99670	0.99487
0.04906	1.00164	1.00047	0.99905	0.99741	0.99558
0.06515	1.00225	1.00105	0.99964	0.99800	0.99618
0.08208	1.00289	1.00171	1.00031	0.99868	0.99682
0.09868	1.00358	1.00237	1.00110	0.99932	0.99748
0.1154	1.00438	1.00318	1.00162	0.99999	0.99812

Table 2. Partial Molar Volume at Infinite Dilution, V_3^0/cm^3·mol^{-1}, for Nicotinic Acid (3) in {Water (1) + PVA (2)}

c_2	V_3^0/cm^3·mol^{-1}				
g·dm^{-3}	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
0	165.3	164.9	164.6	164.5	164.3
0.5007	164.9	164.8	164.5	164.3	164.2
1.0006	164.7	164.6	164.4	164.2	164
2.0003	164.4	164.4	164.3	164	163.9
4.0006	164.1	164.2	164.1	163.8	163.6
6.0004	163.8	163.8	163.7	163.5	163.3

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. The conductivity date was read at least three times at each experimental condition with four digital numbers. The relative error of the measurement was < 0.1 %.

Results and Discussion

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

$$\rho_{123} = \rho_{12} + \alpha m_3 \tag{1}$$

where m_3/mol·kg^{-1} is the molality of nicotinic acid in PVA aqueous solution and ρ_{123} and ρ_{12} represent the density of the solution (1 + 2 + 3) and (1 + 2), respectively. For a given sample series with constant c_2 and different m_3, the value of α can be obtained by a least-squares regression method. The partial molar volume at infinite dilution, V_3^0, can be calculated by

$$V_3^{\ 0} = \frac{M_3}{\rho_{12}} + \frac{1000\alpha}{\rho_{12}^{\ 2}} \tag{2}$$

The values of V_3^0/cm^3·mol^{-1} are shown in Table 2.

Electrical Conductance and the Degree of Dissociation. For the system of nicotinic acid (3) solved in solutions of {water (1) + PVA (2)} with several constant concentrations, c_2 = (0, 1.0006, 2.0003, 4.0007, and 6.0003) g·dm^{-3}, the molar electric conductance (Λ) of nicotinic acid was measured by a conductivity meter at T = (293.15, 298.15, 303.15, 308.15, and 313.15) K. The limiting molar conductance of nicotinic acid in water (Λ^∞) was obtained from literature.[9] The degree of dissociation (β) of nicotinic acid can be calculated by eq 3.

$$\beta = \Lambda/\Lambda^\infty \tag{3}$$

Figure 1 shows the three-dimensional (3D) curve of β−T−c_3 of three sample series, c_2 = (0, 1.006, and 6.0003) g·dm^{-3}, respectively. It clearly shows the effect of T and c_2 on β.

Since the first and the second dissociation constants K_{a1} and K_{a2} of nicotinic acid are widely separated in water (K_{a1}: 10^{-5} and K_{a2}: 10^{-12}),[9] the expected contribution coming from the second dissociation step is negligible, and therefore nicotinic acid can be treated as a monobasic acid.

$$K_a = \frac{c_3\beta^2}{1-\beta}F = \frac{c_3\beta^2}{1-\beta}\frac{f_{H^+}f_{Nic^-}}{f_{HNic}} \tag{4}$$

where K_a is the dissociation constant and f is the activity coefficient. The degree of dissociation β can be successively evaluated for every concentration c_3 by an iterative solution of the quadratic equation.

$$\beta = \frac{1}{2}\left\{-\frac{K_a}{c_3F} + \sqrt{\left(\frac{K_a}{c_3F}\right)^2 + \frac{4K_a}{c_3F}}\right\} \tag{5}$$

where

$$F = \frac{f_{H^+}f_{Nic^-}}{f_{HNic}} \tag{6}$$

In the process of data treatment, F is supposed to be expressed by eq 7, which similar to the Debye−Hückel equation.

$$\ln F = \frac{-F_1\sqrt{c_3}}{1 + F_2\sqrt{c_3}} \tag{7}$$

where F_1 and F_2 are adjustable parameters, which depend on solvent and composition. The values of F_1 and F_2 were evaluated by fitting experimental data using eqs 5 and 7.

On the basis of thermodynamic relations, the effect of temperature on K_a can be expressed by

$$K_a(T) = K_a(T_1)\exp\left[-\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right] \tag{8}$$

where ΔH is the change of enthalpy of dissociation. It varies with temperature and the concentration of PVA, c_2. If the effect of temperature on ΔH is negligible, the effect of c_2 on ΔH can be simply expressed by eq 9. Since c_2 is in a dilute concentration region, a linear approximation was supposed.

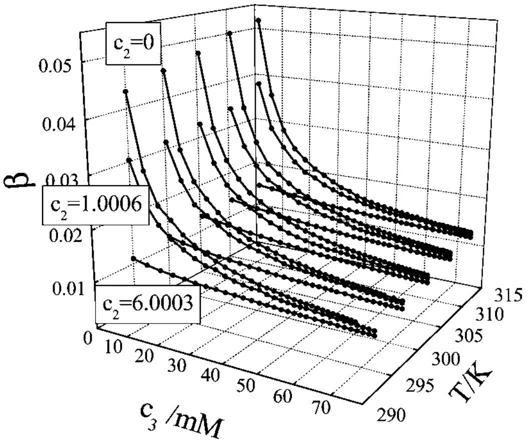

Figure 1. 3D curves of $\beta-T-c_3$ for three sample series of a solution of {water (1) + PVA (2) + nicotinic acid (3)} with a constant concentration of c_2 = (0, 1.0006, and 6.0004) g·dm^{-3}.

$$\Delta H = h_0 + h_1c_2 \tag{9}$$

In eq 9, h_0 represents the enthalpy change in water, and h_1 is a linear coefficient.

Furthermore, at a constant temperature T, the effect of PVA on K_a can be expressed through a linear equation of the Gibbs free energy, ΔG, against c_2.

$$\Delta G = \Delta G^0 + gc_2 \tag{10}$$

where ΔG^0 represents the change of Gibbs free energy in water and g is a linear coefficient. Then, the constant of dissociation K_a at temperature T can be expressed by

$$K_a(T) = \exp(-\Delta G/RT) = \exp(-\Delta G^0/RT)\exp(-gc_2/RT) \tag{11}$$

Combining eqs 8, 9, 10, and 11, we have

$$K_a(T) = K_a^0(T_1)\exp(-gc_2/RT_1)\exp\left[-\frac{(h_0 + h_1c_2)}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right] \tag{12}$$

where $K_a^0(T_1)$ is the dissociation constant at T_1 in pure water.

On the basis of above relations, conductivity data was fitted by the following process. First, data correlation for β to c_3 using eqs 5, 7, and 12 was performed to a binary solution of {water (1) + nicotinic acid (3)}. In this step, parameters F_1, F_2, $K_a^0(T_1)$, and h_0 were obtained by using a nonlinear least-squares method. Then, a data fit was performed to the ternary system. In this step, parameters $K_a^0(T_1)$ and h_0 obtained from binary system were used. F_1 and F_2 coincide with ternary solution, and the mean values of h_1 and g were obtained. Table 3 gives the values of $K_a^0(T_1)$, h_0, h_1, g, F_1, and F_2. Polynomial equations of F_1 and F_2 against c_2 are obtained to express their relation.

$$F_1 = -5.528 + 12.05c_2 + 2.374c_2^2 \tag{13}$$

$$F_2 = 3.144 + 2.720c_2 \tag{14}$$

Viscosity and the B-Coefficients of Viscous Flow. Viscosities of the ternary solution of {water (1) + PVA (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.

$$\eta_r = 1 + A(\beta c_3)^{1/2} + B(1-\beta)c_3 \tag{15}$$

where η_r is the relative viscosity. The A-coefficient, which depend on the interionic force, can be evaluated theoretically by Falkenhagen equation as described in some articles.[10]

$$A = \frac{0.2577\Lambda^0}{\eta_0(\varepsilon T)^{1/2}\lambda_+^0\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2\right] \tag{16}$$

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 coef-

Table 3. Parameters of K_a^0, h_0, h_1, g, F_1, and F_2

c_2 / g·dm^{-3}	F_1 / (mol·dm^{-3})$^{-1/2}$	F_2 / (mol·dm^{-3})$^{-1/2}$	K_a^0 (293.15 K)	g / kJ·mol^{-1}·g^{-1}·dm^3	h_0 / kJ·mol^{-1}	h_1 / kJ·mol^{-1}·g^{-1}·dm^3
0	−4.983	16.14	1.11·10^{-5}	2.958	15.52	1.055
0.5007	1.011	4.505				
1.0006	7.389	4.539				
2.0003	29.29	9.980				
4.0006	80.43	14.55				
6.0004	152.3	18.87				

Table 4. Viscosity, η/mPa·s, of the Solution of {Water (1) + PVA (2) + Nicotinic Acid (3)}

m_3	η/mPa·s				
mol·kg^{-1}	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
c_2/g·dm^{-3} = 0					
0	1.003	0.8904	0.7973	0.7194	0.6530
0.004283	1.004	0.8912	0.7981	0.7201	0.6538
0.006512	1.005	0.8917	0.7985	0.7205	0.6543
0.008188	1.006	0.8923	0.7989	0.7211	0.6547
0.01628	1.007	0.8941	0.8005	0.7224	0.6561
0.03262	1.011	0.8978	0.8035	0.7254	0.6588
0.04903	1.015	0.9012	0.8067	0.7282	0.6610
0.06555	1.018	0.9039	0.8098	0.7312	0.6639
0.08210	1.022	0.9074	0.8127	0.7338	0.6662
0.09871	1.026	0.9109	0.8158	0.7364	0.6686
0.1154	1.029	0.9144	0.8192	0.7395	0.6713
0.1321	1.033	0.9178	0.8225	0.7420	0.6742
c_2/g·dm^{-3} = 0.5007					
0	1.045	0.9260	0.8284	0.7469	0.6771
0.004096	1.047	0.9275	0.8298	0.7484	0.6788
0.008155	1.048	0.9288	0.8310	0.7491	0.6799
0.01630	1.050	0.9305	0.8322	0.7508	0.6809
0.03263	1.054	0.9340	0.8358	0.7538	0.6833
0.04907	1.058	0.9373	0.8386	0.7565	0.6856
0.06552	1.062	0.9413	0.8416	0.7591	0.6883
0.08209	1.066	0.9450	0.8453	0.7623	0.6917
0.09840	1.070	0.9482	0.8485	0.7649	0.6939
0.1154	1.074	0.9516	0.8521	0.7681	0.6965
0.1320	1.078	0.9554	0.8553	0.7718	0.6995
c_2/g·dm^{-3} = 1.0006					
0	1.090	0.9645	0.8613	0.7762	0.7030
0.004112	1.091	0.9652	0.8620	0.7770	0.7040
0.008180	1.092	0.9669	0.8635	0.7778	0.7051
0.01624	1.094	0.9692	0.8656	0.7795	0.7063
0.03267	1.099	0.9725	0.8684	0.7828	0.7092
0.04906	1.103	0.9767	0.8721	0.7859	0.7118
0.06540	1.108	0.9803	0.8754	0.7890	0.7147
0.08203	1.112	0.9844	0.8794	0.7923	0.7180
0.09870	1.116	0.9882	0.8826	0.7957	0.7208
0.1154	1.120	0.9916	0.8859	0.7989	0.7235
c_2/g·dm^{-3} = 2.0003					
0	1.184	1.046	0.9311	0.8372	0.7568
0.004080	1.186	1.047	0.9326	0.8381	0.7580
0.008164	1.187	1.048	0.9336	0.8390	0.7591
0.01632	1.189	1.051	0.9356	0.8408	0.7605
0.03264	1.194	1.055	0.9394	0.8443	0.7632
0.04908	1.199	1.059	0.9431	0.8478	0.7663
0.06554	1.204	1.063	0.9467	0.8513	0.7695
0.08211	1.208	1.067	0.9506	0.8548	0.7726
0.09871	1.213	1.072	0.9541	0.8582	0.7762
0.1154	1.218	1.076	0.9576	0.8618	0.7795
c_2/g·dm^{-3} = 4.0006					
0	1.402	1.231	1.092	0.9764	0.8786
0.004072	1.404	1.232	1.093	0.9778	0.8799
0.008164	1.405	1.234	1.094	0.9795	0.8814
0.01624	1.408	1.236	1.097	0.9811	0.8831
0.03256	1.414	1.241	1.101	0.9849	0.8860
0.04908	1.420	1.246	1.106	0.9887	0.8902
0.06553	1.424	1.251	1.110	0.9923	0.8936
0.08208	1.430	1.256	1.114	0.9963	0.8965
0.09867	1.436	1.261	1.118	1.0007	0.9007
0.1154	1.440	1.266	1.123	1.0048	0.9045
c_2/g·dm^{-3} = 6.0004					
0	1.661	1.451	1.281	1.141	1.023
0.004072	1.662	1.452	1.282	1.141	1.024
0.008172	1.664	1.453	1.284	1.143	1.025
0.01630	1.667	1.456	1.286	1.145	1.027
0.03266	1.673	1.461	1.291	1.149	1.031
0.04906	1.679	1.467	1.296	1.154	1.035
0.06515	1.685	1.473	1.301	1.158	1.039
0.08208	1.691	1.478	1.305	1.163	1.043
0.09868	1.698	1.484	1.311	1.168	1.048
0.1154	1.705	1.491	1.317	1.173	1.052

Table 5. Limiting Molar Conductance of Nicotinic Acid, Λ^0, and the Ions, $\lambda^0(H^+)$ and $\lambda^0(Nic^-)$, and the Dielectric Coefficient of Aqueous Solution ε

T	Λ^0	$\lambda^0(H^+)$	$\lambda^0(Nic^-)$	
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

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

c_2/g·dm^{-3}	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
			A/(dm^3·mol^{-1})$^{1/2}$		
0	0.0316	0.0324	0.0332	0.0340	0.0346
0.5007	0.0303	0.0311	0.0320	0.0327	0.0334
1.0006	0.0291	0.0299	0.0308	0.0315	0.0321
2.0003	0.0267	0.0276	0.0284	0.0292	0.0298
4.0006	0.0226	0.0234	0.0243	0.0250	0.0257
6.0004	0.0191	0.0199	0.0207	0.0214	0.0221
			B/(dm^3·mol^{-1})		
0	0.223	0.228	0.232	0.236	0.241
0.5007	0.236	0.239	0.243	0.246	0.249
1.0006	0.240	0.243	0.245	0.248	0.251
2.0003	0.240	0.244	0.247	0.250	0.254
4.0006	0.236	0.240	0.244	0.249	0.253
6.0004	0.224	0.229	0.235	0.241	0.245

ficient ε of the solvent can be obtained from literature,[9] which are listed in Table 5. The η_0/(Pa·s) is the viscosity of solvent. Using eq 15 to fit viscosity, the *B*-coefficient can be obtained with a standard error less than 0.003 dm^3·mol^{-1}. In fact, because c_3 is located in the region where β is much smaller, the contribution of acid molecules to the *B*-coefficient was just considered. Table 6 gives the values of *A*- and *B*-coefficients.

With the increase in c_2, the *B*-coefficient increases first and then decreases after a top point. It indicates that, with more PVA added into water, less acid is dissociated and the acid moves with more difficulty. With further amounts of PVA added, PVA promotes the solubility and the diffusion of nicotinic acid.

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,

$$\eta_1 = (hN_A/V_{m1})\exp(\Delta\mu_1^{\neq 0}/RT) \qquad (17)$$

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

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

$$\eta_{12} = (hN_A/V_{m12})\exp(\Delta\mu_{12}^{\neq}/RT) \qquad (18)$$

where V_{m12} is the mean molar volume of the solution (1 + 2) and $\Delta\mu_{12}^{\neq}$ is the average free energy of activation for the viscous flow of (1 + 2). Because V_{m12} and η_{12} are measurable variables, then $\Delta\mu_{12}^{\neq}$ can be calculated from eq 18.

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

$$\Delta\mu_{123}^{\neq} = x_{12}\Delta\mu_{12}^{\neq} + x_3\Delta\mu_3^{\neq} \qquad (19)$$

where $\Delta\mu_3^{\neq}$ and $\Delta\mu_{12}^{\neq}$ represent the contribution from solute 3 and solvent (1 + 2), respectively. On the basis of the method of Feakins et al.,[11,12] an equation correlating the *B*-coefficient with the activation free energy is given by eq 20.

$$B = (\nu V_{\mathrm{m12}} - V_3^{\,0}) + (V_{\mathrm{m12}}/RT)(\Delta\mu_3^{\neq} - \nu\Delta\mu_{12}^{\neq}) \tag{20}$$

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 15, the value of $\Delta\mu_3^{\neq}$ can be calculated by eq 20.

If $\Delta\mu_3^{\neq}$ were known at several temperatures, the mole activation enthalpy of solute 3 can be calculated by

$$\mathrm{d}(\Delta\mu_3^{\neq}/T)/\mathrm{d}(1/T)_p = \Delta H_{\mathrm{m3}}^{\neq} \tag{21}$$

The mole activation entropy of solute 3 can be calculated by eq 22.

$$\Delta S_{\mathrm{m3}}^{\neq} = (\Delta H_{\mathrm{m3}}^{\neq} - \Delta\mu_3^{\neq})/T \tag{22}$$

In this work, the $\Delta\mu_{12}^{\neq}$ of the binary solution of {water (1) + PVA (2)} was calculated from their viscosity η_{12}. The V_{m12} is calculated from their density. The segment of PVA is [CH_2−CHOH], and its segment mass is $M_2 = 44.053$. For the convenience of calculation, segment mass was used to substitute the molecular mass to calculate the concentration. Figure 2 shows the curves of $\Delta\mu_{12}^{\neq}$ against c_2. From the linear slope of $\Delta\mu_{12}^{\neq}/T$ against $1/T$, the viscous activation enthalpy, $\Delta H_{\mathrm{m12}}^{\neq}$, was obtained. In Table 7, some activation thermodynamic properties of the viscous flow of PVA aqueous solution are listed.

For ternary solution, $\Delta\mu_3^{\neq}$ was calculated by eq 20. The influence of c_2 on $\Delta\mu_3^{\neq}$ is shown in Figure 3. The activation enthalpy, $\Delta H_{\mathrm{m3}}^{\neq}$, was calculated from the linear slope of $(\Delta\mu_3^{\neq}/T)$ against $(1/T)$, which is shown in Figure 4. The activation entropy was calculated by eq 22. The activation parameters are listed in Table 7. The standard error of the *B*-coefficient is < 0.003 $dm^3 \cdot mol^{-1}$. According to eq 20, the error of $\Delta\mu_3^{\neq}$ is estimated to be 0.4 $kJ \cdot mol^{-1}$. For the linear fit in Figure 4, the standard error is less than 0.00046. Therefore, the linear relationship between $(\Delta\mu_3^{\neq}/T)$ and $(1/T)$ is reasonable. It can be found in Table 7 that most of the values of $\Delta H_{\mathrm{m3}}^{\neq}$ were negative. With the increase in c_2, $\Delta H_{\mathrm{m3}}^{\neq}$ increases first, and then after a top point it decreases. This is the reason why some lines cross in Figure 4.

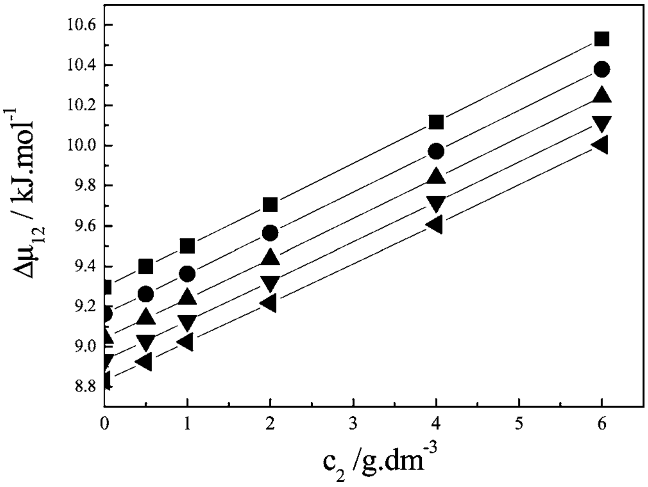

Figure 2. Dependence of the average activation free energy, $\Delta\mu_{12}^{\neq}$, of aqueous PVA solution on the concentration of PVA, $c_2/g \cdot dm^{-3}$, at T = ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ▼, 308.15 K; and left-pointing triangle, 313.15 K.

Table 7. Activation Parameters of Viscous Flow

c_2 / $g \cdot dm^{-3}$		T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
	$\Delta H_{\mathrm{m12}}^{\neq}/kJ \cdot mol^{-1}$			$\Delta\mu_{12}^{\neq}/kJ \cdot mol^{-1}$		
0	16.1	9.29	9.16	9.04	8.93	8.83
0.5007	16.3	9.40	9.26	9.14	9.03	8.92
1.0006	16.5	9.50	9.36	9.24	9.13	9.02
2.0003	16.9	9.70	9.56	9.44	9.32	9.22
4.0006	17.6	10.1	9.97	9.84	9.72	9.61
6.0004	18.3	10.5	10.4	10.2	10.1	10.0
	$\Delta H_{\mathrm{m3}}^{\neq}/kJ \cdot mol^{-1}$			$\Delta\mu_3^{\neq}/kJ \cdot mol^{-1}$		
0	−12.5	59.4	60.7	61.6	63.0	64.3
0.5007	−3.68	61.2	62.2	63.4	64.5	65.6
1.0006	1.14	61.7	62.8	63.8	64.9	65.9
2.0003	−5.06	61.9	63.1	64.0	65.3	66.5
4.0006	−11.3	61.7	62.9	64.2	65.4	66.7
6.0004	−19.9	60.4	61.8	63.3	64.6	65.8

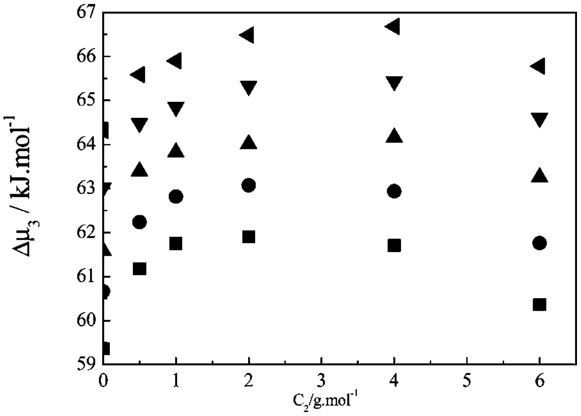

Figure 3. Effect of the concentration of PVA on the $\Delta\mu_3^{\neq}$ at temperatures T = ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ▼, 308.15 K; and left-pointing triangle, 313.15 K.

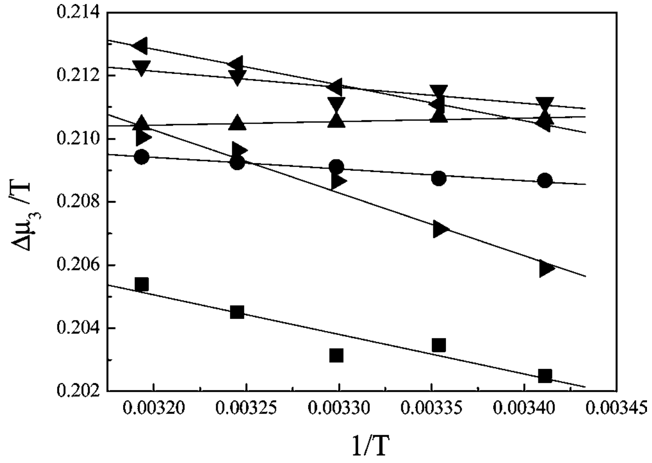

Figure 4. $\Delta\mu_3^{\neq}/T$ against $1/T$ and the linear fit for nicotinic acid in PVA aqueous solution with $c_2/g \cdot dm^{-3}$ = ■, 0; ●, 0.5007; ▲, 1.0006; ▼, 2.0003; left-pointing triangle, 4.0006; right-pointing triangle, 6.0004.

The effect of c_2 on activation parameters $\Delta H_{\mathrm{m3}}^{\neq}$, $T\Delta S_{\mathrm{m3}}^{\neq}$, $\Delta H_{\mathrm{m12}}^{\neq}$, and $T\Delta S_{\mathrm{m12}}^{\neq}$ is shown in Figure 5. Because of the small change of the values of $T\Delta S_{\mathrm{m3}}^{\neq}$ and $T\Delta S_{\mathrm{m12}}^{\neq}$ at different temperatures, only the data at 298.15 K are shown. Figure 5 shows that $\Delta H_{\mathrm{m12}}^{\neq}$ and $T\Delta S_{\mathrm{m12}}^{\neq}$ change little with c_2. This observation indicates that the addition of PVA does not produce apparent change in the medium structure. Figure 5 also shows that $\Delta H^{\neq}{}_{\mathrm{m3}}$ and $T\Delta S_{\mathrm{m3}}^{\neq}$ are mainly negative. With the increase in c_2, they increase first and then decrease after a top point. The negative $\Delta S_{\mathrm{m3}}^{\neq}$ may be the reflection that the opposite ions interact to form molecules.

Conclusion

With the addition of PVA into water, the dissociation and molecular diffusion of nicotinic acid becomes difficult, and $\Delta\mu_3^{\neq}$

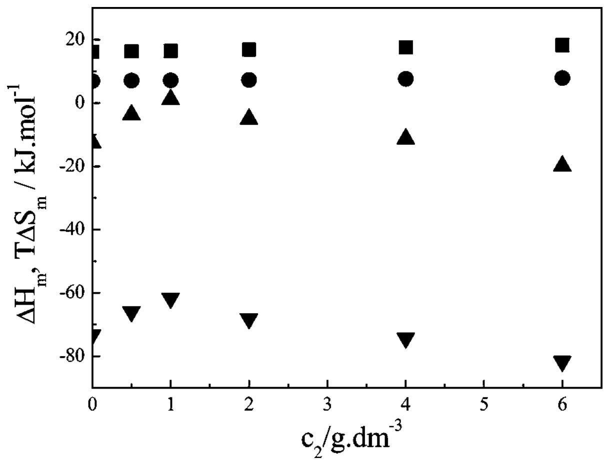

Figure 5. Effect of the concentration of PVA on the activation parameters of ■, $\Delta H^{\neq}_{m12}$/kJ·mol^{-1}; ●, $T\Delta S^{\neq}_{m12}$/kJ·mol^{-1}; ▲, $\Delta H^{\neq}_{m3}$/kJ·mol^{-1}; and ▼, $T\Delta S^{\neq}_{m3}$/kJ·mol^{-1}.

increases. With further amounts of PVA added, the capacity of PVA to promote the solubility of nicotinic acid appears. It leads to the decrease of $\Delta\mu_3^{\neq}$ after a top point and indicates the enhancement of the diffusion of the nicotinic acid.

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