Density, Partial Molal Volume, Refractive Index, Polarizability, and Viscosity of Concentrated and Saturated Aqueous Solutions of Rochelle Salt

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The density, refractive index, and viscosity of aqueous solutions of Rochelle salt were measured as a function of its concentration up to saturation at 25°C. Tha apparent partial molal volume and polarizability of the solute obtained from the densities and refractive indices were nearly equal to the molar volume and polarizability of crystalline Rochelle salt. The logarithm of the viscosity was linearly changed against the mole fraction of crystalline Rochelle salt in the aqueous solution up to saturation. The density of the saturated solution was measured as a function of temperature between 10° and 60°C, and the apparent partial molal volume of the solute in the saturated solution was obtained in the above temperature range. The volume was smaller than the molar volume of crystalline Rochelle salt below about 26°C and slightly larger above the temperature. The activation energies obtained from viscosity were, respectively, 3.78 and 5.02 kcal/mol in 1.0 and 2.5*M* solution in the temperature range between 20° and 40°C.

Growth of crystals from aqueous solutions is a well-known and important technique in the field of crystal growth. But there is little known about concentrated and saturated solutions: which species cultivates a crystal in the solution, or how should solvation be described? Of all problems concerning crystal growth from solutions, structure of solutions may play a crucial role in determining the rate of crystal growth and crystal habit (*4*).

In an attempt to understand concentrated and saturated aqueous solutions, the density, refractive index, and viscosity of aqueous solutions of Rochelle salt (Na-K $C_4H_4O_6 \cdot 4H_2O$) were measured as a function of its concentration up to the saturation. The apparent partial molal volume (*2*) and molar polarizability of the solute were obtained by using the densities and refractive indices as a function of concentration. The apparent partial molal volume of the solute in the saturated solution was obtained as a function of temperature between 10° and 60°C. The activation energies of viscosity were obtained in 1.0 and 2.5*M* solutions in the temperature range between 20° and 40°C.

Experimental

All solutions measured here were prepared by distilled water and recrystallized particles of Rochelle salt which were dried with caution to prevent efflorescence of the salt.

The densities and viscosities were measured, respectively, with a pycnometer and an Ostwald viscosimeter in a regulated chamber within ±0.01°C (temperature fluctuation) and with an accuracy of ±0.1°C (in the sense of the reproducibility of temperature setting). The experimental errors in density and viscosity were estimated to ±0.0002 g/cm^3 and ±0.001 × 10^{-2} poise, respectively. The solutions to be measured were put in the chamber several days before measurements.

The (relative) refractive index of the solution was measured with a differential refractometer with Hg:5461 Å at 25.0° ± 0.1°C. The experimental error was estimated to ±0.00003.

Results and Discussion

Density and partial molal volume. The density of the Rochelle salt solution, ρ, is shown in Table I as a function of its concentration, C (in molarity), and given by Equation 1 after application of the least-squares fitting method to the measured values.

$$\rho = 0.99758 + 0.13723\,C - 0.00495\,C^2 \qquad (1)$$

The apparent partial molal volume (*2*) defined by

$$\phi = (V - N_1 \bar{V}_1^\circ)/N_2 \qquad (2)$$

is plotted against C in Figure 1. Here, V is the volume of the solution containing N_1 moles of water and N_2 moles of crystalline Rochelle salt, and $\bar{V}_1^\circ$ is the molar volume of pure water at a given temperature. The partial molal volume of the solute (*2*) given by

$$\bar{V}_2 = \partial V/\partial N_2 = \phi + N_2 \partial\phi/\partial N_2 \qquad (3)$$

Table I. Refractive Index and Density of Rochelle Salt Solution as Function of Its Concentration
Refractive indices measured by differential refractometer with Hg:5461 Å at 25.0° ± 0.1°C and densities at 25.0° ± 0.01°C

Molarity	Refractive index	Density, g/cm^3
0.1 ± 0.05%	1.33573 ± 0.00003	1.0110 ± 0.0002
0.2	1.33847	1.0248
0.3	1.34178	1.0385
0.4	1.34450	1.0522
0.5	1.34760	1.0650
0.6	1.35032	1.0781
0.7	1.35318	1.0921
0.8	1.35592	
0.9	1.35868	
1.0	1.36196	1.1296
1.1	1.36477	
1.2	1.36750	
1.3	1.37034	
1.4	1.37244	
1.5	1.37498	1.1918
1.6	1.37760	
1.7	1.37989	
1.8	1.38267	
1.9	1.38501	
2.0	1.38776	1.2517
2.1	1.39044	
2.2	1.39282	
2.3	1.39541	
2.4	1.39721	
2.5	1.39994	1.3106
2.525 (saturation)		1.3121

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is calculated by using Equation 1 as

$$\bar{V}_2 = 145.00 + 9.90\,C \qquad (4)$$

Since the density of crystalline Rochelle salt is reported as 1.766, 1.775, and 1.780 (*3*), its molar volume, $\bar{V}^{\circ}_{2:\text{crystal}}$, is estimated to 159.8, 159.0, and 158.6 cm³/mol, respectively.

The density of the saturated solution of Rochelle salt as a function of temperature is shown in Table II. The apparent partial molal volume of the solute in the saturated solution is obtained as a function of temperature (Figure 2). The volume is smaller than $\bar{V}^{\circ}_{2:\text{crystal}}$ below about 26°C and slightly larger than it above the temperature.

Polarizability. The refractive index, n, of the solution containing N_1 moles of water and N_2 moles of crystalline Rochelle salt per cm³ is given by the Lorentz-Lorenz relation:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}(N_1\alpha_1 + N_2\alpha_2) \qquad (5)$$

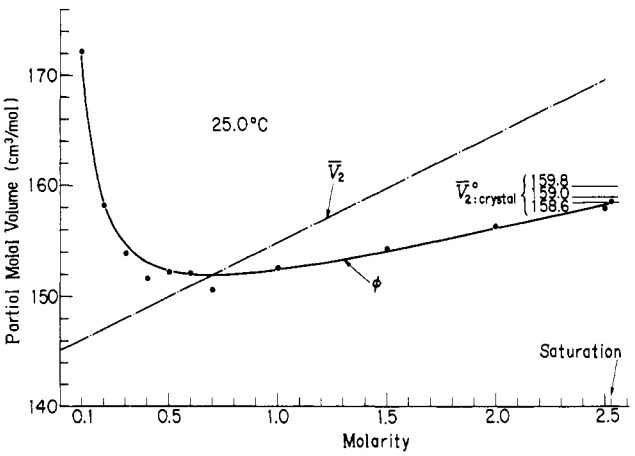

Figure 1. Apparent partial molal volume, ϕ, and partial molal volume, $\bar{V}_2$, of solute as function of concentration of crystalline Rochelle salt

•: Apparent partial molal volume obtained from measured values of density. Solid line: volume calculated from Equation 1. Broken line: $\bar{V}_2$ given by Equation 4. Molar volume of Rochelle salt crystal shown by $\bar{V}^{\circ}_{2:\text{crystal}}$

Table II. Density of Saturated Solution of Rochelle Salt as Function of Temperature

Temp, °C	Density, g/cm³
10.0 ± 0.1	1.2351 ± 0.0002
20.0	1.2851
25.0	1.3121
30.0	1.3392
40.0	1.4072
50.0	1.4696
60.0	1.5060

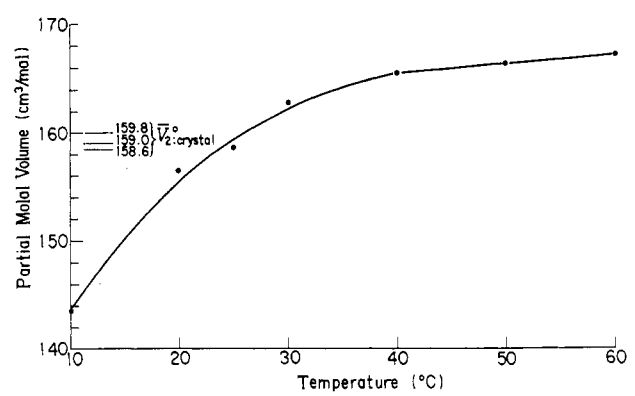

Figure 2. Apparent partial molal volume of solute in saturated solution as function of temperature

Table III. Polarizabilities of Solvent, α_1, and Solute, α_2, in Aqueous Solutions of Rochelle Salt

Concn $(C + C')/2$, molarity	Polarizability, cm³/mol			
	0.1 mol interval		0.5 mol interval	
	α_1	α_2	α_1	α_2
0.15	0.886	10.83		
0.25	0.883	11.65		
0.35	0.887	10.93	0.8854	11.178
0.45	0.883	11.45	0.8845	11.251
0.55	0.887	11.01	0.8858	11.150
0.65	0.885	11.23	0.8850	11.196
0.75	0.886	11.15	0.8848	11.281
0.85	0.885	11.18	0.8835	11.337
0.95	0.874	11.80	0.8832	11.341
1.05	0.884	11.32	0.8818	11.397
1.15	0.885	11.27	0.8835	11.280
1.25	0.881	11.41	0.8873	11.161
1.35	0.903	10.68	0.8877	11.158
1.45	0.887	11.16	0.8895	11.103
1.55	0.883	11.27	0.8896	11.130
1.65	0.894	10.99	0.8859	11.204
1.75	0.874	11.47	0.8832	11.278
1.85	0.890	11.11	0.8815	11.320
1.95	0.871	11.50	0.8851	11.208
2.05	0.873	11.47	0.8793	11.359
2.15	0.927	10.52	0.8819	11.287
2.25	0.833	12.06	0.8811	11.316
2.35	0.913	10.84		
2.45	0.861	11.58		
Mean value	0.88_4	11.2_4	0.884	11.24
Deviation	±0.02	±0.35	±0.003	±0.09

Table IV. Viscosity of Rochelle Salt Solution as Function of Its Concentration at 25.0° ± 0.01°C

Concn, molarity	Viscosity, poise
0.01	$(0.934 \pm 0.001) \times 10^{-2}$
0.20	0.989
0.30	1.037
0.40	1.083
0.50	1.140
0.60	1.197
0.80	1.335
0.90	1.424
1.00	1.497
1.10	1.588
1.40	1.927
1.50	2.047
1.60	2.168
1.80	2.552
2.00	2.907
2.20	3.477
2.40	4.101
2.50	4.444

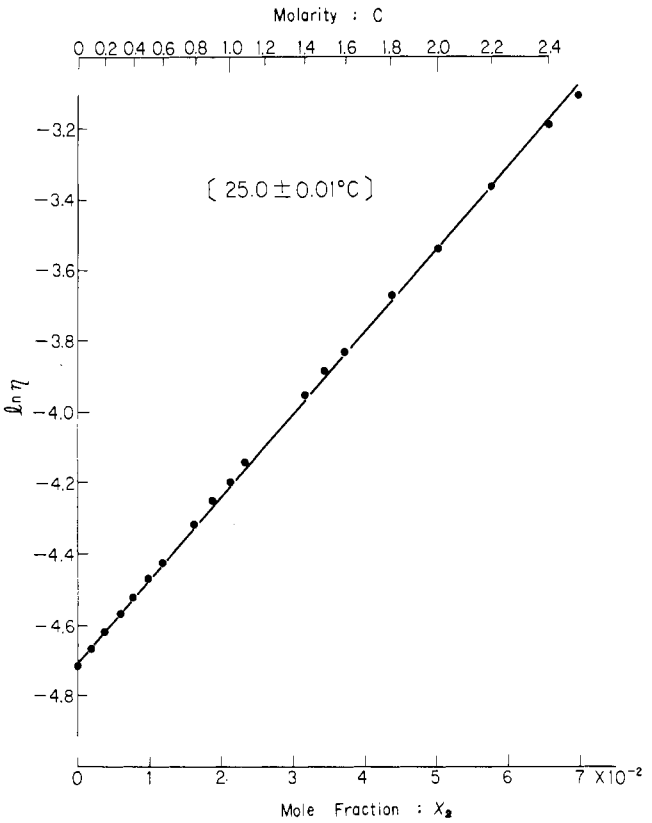

Figure 3. Logarithm of viscosity of solution against mole fraction of crystalline Rochelle salt in solution

Table V. Viscosities of 1.00 and 2.50*M* Solutions of Rochelle Salt as Function of Temperature

Temp, °C	Viscosity, poise	
	Concn, molarity	
	1.00*M*	2.50*M*
20.0	1.61 ± 0.03	
25.0	1.49	3.41 ± 0.03
30.0	1.33	2.90
35.0	1.18	2.53
40.0	1.08	2.28

where α_1 and α_2 are molar polarizabilities of the solvent and solute, respectively. The refractive index, n', of the solution containing N_1' and N_2' mol/cm^3 will be given by

$$\frac{n'^2 - 1}{n'^2 + 2} = \frac{4\pi}{3}(N_1'\alpha_1' + N_2'\alpha_2') \qquad (6)$$

Therefore, α_1 and α_2 are obtained from Equations 5 and 6. They are listed in Table III by using the refractive indices in Table I and Equation 1 in order to get N_1. In the table the polarizabilities are calculated at an interval of 0.1 and 0.5*M* (in molarity) and listed at the row of the mean concentration: $(C + C')/2$.

The polarizability of pure water is 0.88617 cm^3/mol using n = 1.333938 at 5461 Å and at 25.0°C (*1*), which is equal to α_1 in Table III within the experimental error. The polarizability of Rochelle salt crystal is estimated to 11.12 cm^3/mol by using ρ = 1.766 and the mean refractive index given by

$$\bar{n} = (n_\alpha + n_\beta + n_\gamma)/3 = 1.4947$$

which is estimated by n_α = 1.4932, n_β = 1.4950, n_γ = 1.4990 at 5270 Å, and n_α = 1.4900, n_β = 1.4918, n_γ = 1.4954 at 5890 Å, because of fairly small anisotropy in the optical indices. The polarizability of Rochelle salt crystal coincides with α_2 in Table III.

Viscosity. The viscosity, η, of the solution is shown in Table IV, and ln η is plotted against the mole fraction of crystalline Rochelle salt: $X_2 = N_2/(N_1 + N_2)$ in Figure 3. In the figure all the data are on a straight line which is given by

$$\ln \eta = -4.696 + 23.14\, X_2 \qquad (7)$$

The correlation between the observed viscosities and the line given by Equation 7 is 0.9996. Figure 3 is the only linear relationship between viscosity and concentration in the whole range of concentration until saturation.

The viscosity in the solutions of 1.0 and 2.5*M* was measured in the temperature range between 20° and 40°C and is shown in Table V. The activation energies of 1.0 and 2.5*M* solutions are, respectively, 3.78 and 5.02 kcal/mol in the temperature range.

Acknowledgment

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Nomenclature

C = concentration, molarity
N_1 = mole number of solvent water per 1 cm^3 solution
N_2 = mole number of crystalline Rochelle salt in the 1 cm^3 solution
n = refractive index of the solution
V = volume of the solution
$\bar{V}_1^\circ$ = molar volume of pure water
$\bar{V}_2$ = partial molal volume of the solute
X_2 = mole fraction of crystalline Rochelle salt in the solution: $N_2/(N_1 + N_2)$
α_1 and α_2 = molar polarizabilities of solvent and solute, respectively, cm^3/mol
ρ = density of the solution, g/cm^3
ϕ = apparent partial molal volume of the solute
η = viscosity of the solution, poise

Literature Cited

(1) Dorsey, N. E., "Water-Substance," p 281, Hafner, New York, N.Y., 1968.
(2) Millero, F. J., "Water and Aqueous Solutions," Chap. 13, R. A. Horne, Ed., Wiley-Interscience, New York, N.Y., 1972.
(3) Miyake, S., "Rochelle Salt Crystal," (in Japanese), p 8, Oyama-shoten, Tokyo, Japan, 1949.
(4) Troost, S., *J. Cryst. Growth*, **13/14**, 449 (1972).

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