Journal of Chemical and Engineering Data, Vol. 24, No. 3, 1979 **213**

Density and Compressibility of Solutions of $NaClO_3$, $NaNO_3$, KNO_3, and $RbNO_3$ in the Mixed Solvent $C_6H_5NH_3Cl$ (1.0001 *m*)–H_2O at 30 °C

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Density and compressibility of solutions of nitrates and chlorates are measured in the mixed solvent $C_6H_5NH_3Cl$ (1.0001 *m*)–H_2O at 30 °C. The ionic volumes are compared with the corresponding values in other solvents.

Introduction

As a part of our current research on the behavior of type MXO_3 salts in different solvents (*1*, *2*, *5*), in the present paper the density and isoentropic compressibility values are reported concerning the solutions of $NaClO_3$, $NaNO_3$, KNO_3, and $RbNO_3$ in the mixed solvent $C_6H_5NH_3Cl$ (1.0001 *m*)–H_2O. The bromates and iodates were not studied owing to the unstability of corresponding solutions. The salts employed are composed by spheric and electrostrictive cations and planar anions with a high component of disordered volume (*1*, *5*).

Experimental Section

The pycnometric and dilatometric methods previously described (*5*) were employed. These methods enabled us to calculate the apparent molar volume, the first according to

$$\varphi_V = 1000(d^0 - d)/mdd^0 + M_2/d \qquad (1)$$

the second according to

$$\varphi_{V,\mathrm{fin}} = \varphi_{V,\mathrm{st}} - \Delta V/n_2 \qquad (2)$$

The viscosity measurements were performed by means of a Höppler viscosimeter manufactured by VEB Freital, DDR, whose details were given in a previous note (*3*); the fall-tube was on a 10° slope with respect to the vertical of the base plane and was enclosed in a jacket through which circulated thermostated water, originating from an ultrathermostat with exterior circulation. The viscosimeter was thermostated to ±0.05 °C. The fall time of the ball was measured with a chronometer to 0.1 s. Each measurement was repeated several times and the fall time agreed within 0.1 s. The viscosity is given by

$$\eta = k\bar{t}(d_{\mathrm{ball}} - d_{\mathrm{soln}}) \qquad (3)$$

where the constants k and d_{ball} are certified; the lining up of the viscosimetric systems was controlled by measuring the fall time in bidistilled, deaerated, and filtered water and in some oils of guaranteed viscosity, furnished by the same manufacturing firm. The agreement is within 1%. The isoentropic compressibility data were obtained via ultrasonic velocity according to the equation (*11*)

$$\beta_s = 1/u^2d \qquad (4)$$

An ultrasonic interferometer IPPT-PAN (Warszawa) was employed; it consisted of a transmitting part, a receiving part, a minima counter circuit, and an oscilloscope. The pulse method was employed and was described in previous notes (*4*, *6*). The calibration was previously reported (*6*). Merck high purity chemicals were employed without further purification and were dried under dynamic vacuum at a temperature of ≃70 °C. Bidistilled and deaerated water was employed.

Table I. Experimental Values of Density, Apparent Molar Volumes, Isoentropic Compressibility, and Viscosity of Solutions of $C_6H_5NH_3Cl$ in Water at 30 °C

C, mol/L	*d*, g/mL	φ_V, mL/mol	$10^6\beta_s$, bar^{-1}	η, cP
0.0756		103.7		
0.0992		103.7		
0.4953	1.008 50	104.1	41.6	0.92
0.9019	1.018 81	104.4	39.4	1.06
1.6788	1.037 86	104.9	36.5	1.26
2.5459	1.057 85	105.6	34.3	1.62
2.8019	1.063 51	105.8	33.7	1.74
3.6780	1.081 89	106.6	32.2	2.34
3.8561	1.085 66	106.7	31.9	2.50

Results

Solutions of $C_6H_5NH_3Cl$ in H_2O. The experimental values of density, compressibility, and viscosity of $C_6H_5NH_3Cl$–H_2O mixtures and the apparent molar volume calculated are given in Table I. The Redlich equation (*12*, *13*) generally is employed to fit the experimental data of φ_V; in this equation the coefficient of $C^{1/2}$ is the theoretical slope, computable from the Debye–Hückel theory, and the coefficient of C is an empirical parameter; in the present case an equation of higher order is necessary

$$\varphi_V - 1.956\sqrt{C} = 103.3 - 0.9135C + 0.2132C^2 \qquad (5)$$

with a standard deviation of $\sigma = 0.17$. The Jones–Dole equation (*9*) is employed generally in order to express viscosity values of dilute solutions, but in the aqueous solutions of $C_6H_5NH_3Cl$ a higher order equation is necessary

$$(\eta - \eta^0)/\eta^0\sqrt{C} = 0.476 - 0.664\sqrt{C} + 0.490C \qquad (6)$$

with a standard deviation of $\sigma = 0.03$.

A quadratic equation fits the compressibility data (standard deviation $\sigma = 0.14$)

$$\beta_s 10^6 = 43.9 - 5.235C + 0.559C^2 \qquad (7)$$

Solutions of MXO_3 Salts in 1.0001 m $C_6H_5NH_3Cl$. The experimental results of density and compressibility are reported in Table II. The molar volumes are expressed following the Masson equation (*10*)

$$\varphi_V = \varphi_V^0 + S_V\sqrt{C} \qquad (8)$$

because the theoretical slope for the mixed solvent is not known; a linear equation in C is calculated for the compressibility data of solutions of MXO_3 in the mixed solvent. The parameters and the standard deviation are given in Table III.

Discussion

The φ_V value extrapolated to $C = 0$ (eq 5) may be used in order to calculate the volume of $C_6H_5NH_3^+$ employing $\varphi_V(\mathrm{NaCl})$ at 30 °C (*8*) and $\varphi_V(\mathrm{Na^+})$ (*5*); the value obtained (80.9 mL/mol)

0021-9568/79/1724-0213$01.00/0

Table II. Experimental Values of Density and Isoentropic Compressibility of Solutions of $NaClO_3$, $NaNO_3$, KNO_3, and $RbNO_3$ in Mixed Solvent $C_6H_5NH_3Cl$ (1.0001 *m*)-H_2O

C, mol/L	d, g/mL	$10^6\beta_S$, bar^{-1}	
0.0915	1.024 91	39.2	$NaClO_3$
0.1625	1.029 62	38.8	
0.2528	1.035 60	38.5	
0.3625	1.042 85	38.3	
0.0921	1.023 65	39.1	$NaNO_3$
0.1624	1.027 34	38.9	
0.2241	1.030 56	38.7	
0.3046	1.034 83	38.5	
0.3629	1.037 82	38.2	
0.0915	1.024 16	39.1	KNO_3
0.0917	1.024 14	39.2	
0.1620	1.028 26	38.9	
0.2523	1.033 49	38.7	
0.3614	1.039 80	38.3	
0.0914	1.027 95	39.2	$RbNO_3$
0.0923	1.028 06	39.2	
0.1618	1.034 90	38.9	
0.2519	1.043 89	38.6	

Table III. Parameters of the Masson Equation and of the Equation $\beta_S = \beta_S{}^0 + a'C$, Concerning the Solutions of MXO_3 Salts in Mixed Solvent $C_6H_5NH_3Cl$ (1.0001 *m*)-H_2O

salt	$\varphi_V{}^0$	S_V	σ	$10^6\beta_S{}^0$, bar^{-1}	$-a'$	σ
$NaClO_3$	38.8	0.941	0.01	39.4	3.24	0.11
$NaNO_3$	31.6	0.711	0.09	39.4	3.20	0.06
KNO_3	41.7	0.858	0.10	39.4	3.10	0.06
$RbNO_3$	46.7	0.529	0.24	39.5	3.78	0.03

is 10% lower than the value calculated as a sphere of radius $r = (a^2 + b^2 - 2ab\cos\alpha)^{1/2}$ (a = distance between the center of aromatic ring and the N center; b = bond length NH; α = bond angle CNH). The dead space for it is an important component of $V^0(C_6H_5NH_3{}^+)$. The parabolic trend of $\varphi_V - 1.956C^{1/2}$ vs. C with a minimum around C = 1 M points to the probable existence of two effects on $\bar{V}$ ($C_6H_5NH_3Cl$): electrostrictive and cagelike.

As can be seen from the eq 6 and 7 beyond concentration 1 *m* also the viscosity increases more and the compressibility decreases less rapidly. The $\varphi_V{}^0$ of the salts examined in this solvent is higher than $\varphi_V{}^0$ in water, and $\Delta\varphi_V{}^0 = \varphi_{V,solv}{}^0 - \varphi_{V,water}{}^0$ is 3.1 ($NaNO_3$), 2.7 (KNO_3), 2.9 ($RbNO_3$), and 2.8 ($NaClO_3$); these values are lower than those corresponding to the other solvent examined (LiCl 12 *m*) (*2*): 5.7 (KNO_3), 5.9 ($RbNO_3$). From the two sets, in $C_6H_5NH_3Cl$ (1.0001 *m*)-H_2O and in LiCl (12 *m*)-H_2O (*2*), we see that $\Delta\varphi_V{}^0$ depends principally on the solvent employed and is roughly independent of the solute.

The slopes of the straight lines β_s/C concerning the five salts studied are intermediate between the corresponding values of solutions in H_2O and in LiCl (12 *m*)-H_2O (*2*); this fact may be ascribed to a more compact structure of the solvent LiCl (12 *m*)-H_2O in comparison with the corresponding one of $C_6H_5NH_3Cl$ (1.0001 *m*)-H_2O and H_2O. The Glueckauf method (*7*), modified and controlled (*2*) in order to express (a) the dead space as Kr^2 instead of an additive term of the radius and (b) the electrostriction as Az^2/r instead of $Az^2/\bar{r}$, is applied to the nitrates $\varphi_V{}^0$.

$$\varphi_V{}^0 = (4/3)\pi r^3 N + Kr^2 - Az^2/r + \varphi_V{}^- \qquad (9)$$

It gives the following values of A, K, and $\varphi_V{}^-$: $A = 3.6_5$ ($\pm$0.6) (Å mL)/mol; $K = 6.6_5$ ($\pm$0.3) mL/(mol Å^2); $\varphi_V(NO_3{}^-)$ = 26.8 ($\pm$0.7) mL/mol. From the additivity law of $\varphi_V{}^0$, the values of $\varphi_V(ClO_3{}^-)$, $\varphi_V(Na^+)$, $\varphi_V(K^+)$, and $\varphi_V(Rb^+)$ may be calculated: 34.0 ($ClO_3{}^-$), 4.8 (Na^+), 15.0 (K^+), 20.0 (Rb^+) mL/mol. It is noteworthy that $\varphi_V{}^+$ is increasing and $\varphi_V{}^-$ is decreasing in the direction LiCl (12 *m*), H_2O, and $C_6H_5NH_3Cl$ (1.0001 *m*) and that in the same way the electrostriction constant, calculated by the same method, decreases; this last parameter being dependent on the local deformability of the solvent, it may be concluded that the electrostriction and disorder volumes increase with increasing deformability of the solvent.

Glossary

φ_V	apparent molar volume; $\varphi_V{}^0$, $\varphi_V{}^+$, $\varphi_V{}^-$ are values extrapolated to C = 0, of the cation, of the anion, respectively
$\varphi_{V,st}$, $\varphi_{V,fin}$	apparent molar volume of starting and final solutions, respectively
$\varphi_{V,solv}$	apparent molar volume of the salt in a solvent
$\varphi_{V,water}$	apparent molar volume of the salt in water
d	density; d^0 is d extrapolated to C = 0
η	viscosity; η^0 is η extrapolated to C = 0
M_2	molecular weight of the solute
$\bar{t}$	mean fall time
β_s	adiabatic compressibility; $\beta_s{}^0$ is β_s extrapolated to C = 0
u	ultrasonic velocity
C	molarity
m	molality
N	Avogadro's number
r	ionic radius
ΔV	contraction occurring in the dilatometric measurement
n_2	number of molecules of solute contained in the concentrated solution, that dilutes during a dilatometric measurement
k	constant relating viscosity to the fall time and density of the solution
σ	standard deviation
S_V	slope in the Masson equation
$\bar{V}$	molar volume
K	constant in the expression of dead space associated to an ion
A	constant of the electrostriction law
a'	slope in the equation $\beta_s = \beta_s{}^0 - a'C$
$\bar{r}$	distance between the center of the ion and the center of the water dipole

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Received for review September 11, 1978. Accepted January 22, 1979. Thanks are due to CNR (Rome) for financial support.