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Partial Molal Volumes, Expansibilities, and Compressibilities of Aqueous KSCN Solutions from 15 to 35 °C

Harald Hölland* and Ove Jan Kvammen

Department of Chemistry, University of Bergen, N-5014 Bergen U., Norway

The densities and isentropic compressibilities of aqueous solutions of KSCN have been measured from 15 to 35 °C. Partial molal volumes, partial molal expansibilities, and partial molal compressibilities have been calculated. The values at 25 °C are 49.62 $cm^3\ mol^{-1}$, 0.15 $cm^3\ mol^{-1}\ K^{-1}$, and -18.0×10^{-4} $cm^3\ mol^{-1}\ bar^{-1}$, respectively. The partial molal volumes do not agree well with literature values. However, it is strongly believed that the present results are correct.

Introduction

In his review of partial molal volumes of electrolytes in aqueous solution, Millero (*1*) quotes Halasey (*2*) for data on KSCN. Halasey's work appears to be a thorough investigation covering several other electrolytes and a temperature range from 5 to 30 °C. For the other electrolytes there is good agreement between Halasey's values and others workers', but for KSCN the only other value cited is at 25 °C (*3*), and at infinite dilution it is given as 49.0 $cm^3\ mol^{-1}$ compared to Halasey's value of 44.70 $cm^3\ mol^{-1}$.

In connection with other work the partial molal volume of KSCN at infinite dilution was needed. The discrepancies between the two values mentioned above, however, made it necessary to carry out new measurements in order to settle the issue. It was thus found worthwhile to make a thorough investigation and also include the partial molal compressibility and expansibility.

Experimental Section

KSCN was from Merck and was their best quality. It was dried in vacuo at 140 °C for at least 24 h. In order to check the purity, we titrated sample solutions with $AgNO_3$ according to Volhard's method (*4*). The results showed 99.8% KSCN. KSCN of Baker's analyzed quality was also tested. The densities of aqueous solutions were equal irrespective of origin.

The densities were measured by a Paar digital vibrating densitometer, DMA 601. It was calibrated at each temperature by measuring the vibration frequencies when filled with water and air, respectively. The isentropic compressibilities were evaluated from the speed of sound in the solutions as measured by the "singaround" method. The temperature was controlled to better than ±0.004 °C in both cases, as measured with a Hewlett-Packard quartz thermometer.

Results and Discussion

The measured densities and compressibilities are given relative to pure water in Table I.

The apparent molal volumes have been calculated by the usual equation (*5*). They have been plotted in Figure 1 according to the Redlich equation (*6*):

$$V_{\varphi} = V_{\varphi}^{0} + S_{v}\sqrt{c} + b_{v}c \qquad (1)$$

Here the molar unit is used. S_v is thus the Debye–Hückel limiting law coefficient and b_v an adjustable parameter providing a measure of deviation from the limiting law.

The partial molal volume of KSCN at infinite dilution and the deviation parameter are presented in Table II. For comparison the data of Halasey (*2*) are also presented; b_v has been calculated from the data given. The discrepancies are large. However, we firmly believe that our data are the correct ones. Our value at 25 °C is in reasonable agreement with that of Fajans and Johnson (*3*). Furthermore, the b_v values calculated on the basis of Halasey's data are extremely large for such a simple 1:1 electrolyte. If we take the b_v values of NaCl, for which Millero (*7*) has provided accurate data, it can be seen that our data on KSCN compare very well with those of NaCl (0.16 and −0.37 at 15 °C, −0.39 and 0.05 at 25 °C, and −0.61 and −0.13 at 35 °C for KSCN and NaCl, respectively). b_v values of simple 1:1 electrolytes should be expected to be of the same order of magnitude. As Millero (*7*) points out, the deviations from the limiting law must arise from cation–cation (or anion–anion) interactions, on one hand, and cation–anion interactions on the other. It appears that positive deviations are due largely to cation–anion interactions and negative deviations due to cation–cation (anion–anion) interactions. Halasey's large and positive b_v values thus suggest a relatively high degree of ion pairing in aqueous KSCN. This does not seem likely. Further, there is no evidence for such ion pairing from, for instance, conductance measurements; see the tabulated values of 1:1 electrolytes given by Parsons (*8*). In fact, by comparison of our b_v data on KSCN with those of NaCl, it appears that KSCN is even less likely than NaCl to form ion

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Table I. Densities and Isentropic Compressibilities of KSCN in Aqueous Solution[a]

	$10^3(d - d_0)$,[b] g cm^{-3}					$10^6(\beta_{0,s} - \beta_s)$,[c] g cm^{-3} bar^{-1}				
molality	15 °C	20 °C	25 °C	30 °C	35 °C	15 °C	20 °C	25 °C	30 °C	35 °C
0.005 61	0.276	0.272	0.266	0.264	0.257					
0.009 97	0.488	0.482	0.472	0.468	0.458					
0.019 89	0.973	0.959	0.939	0.930	0.915	0.105	0.096	0.088	0.082	0.080
0.050 62	2.467	2.424	2.381	2.350	2.321	0.264	0.244	0.227	0.209	0.195
0.063 94	3.115	3.061	3.003	2.962	2.923	0.331	0.305	0.281	0.262	0.247
0.099 07	4.802	4.714	4.631	4.568	4.507	0.506	0.462	0.431	0.406	0.378
0.196 41	9.442	9.268	9.110	8.980	8.862	0.996	0.914	0.849	0.792	0.738
0.276 95	13.218	12.976	12.757	12.578	12.426	1.389	1.273	1.180	1.105	1.031
0.404 45	19.097	18.761	18.448	18.195	17.964	1.987	1.823	1.691	1.584	1.480
0.503 72	23.598	23.185	22.807	22.491	22.207	2.446	2.249	2.089	1.944	1.834

[a] d_0 is the density of water (*11*); $\beta_{0,s}$ is the isentropic compressibility of water (*12*). [b] ±0.003. [c] ±0.001.

Table II. Partial Molal Volumes and Expansibilities of KSCN in Aqueous Solution Including the Deviation Parameters from the Limiting Law Eq 1

	$V^0{}_2$, cm^3 mol^{-1}		b_V, cm^3 mol^{-2} dm^3		
t, °C	this work[a]	ref 2	this work	ref 2[b]	$E^0{}_2$,[c] cm^3 mol^{-1} k^{-1}
15.0	47.88	42.66	0.16	11.1	0.19
20.0	48.75	43.77	0.00	10.7	0.17
25.0	49.62	44.70	−0.39	10.5	0.15
30.0	50.25	45.53	−0.45	10.2	0.13
35.0	50.85		−0.61		0.11

[a] ±0.10. [b] Calculated from the data in ref *2*. [c] ±0.02. Calculated from the equation $V^0{}_2 = -193.35 + 1.4797T - 0.00223T^2$ derived by the method of least squares.

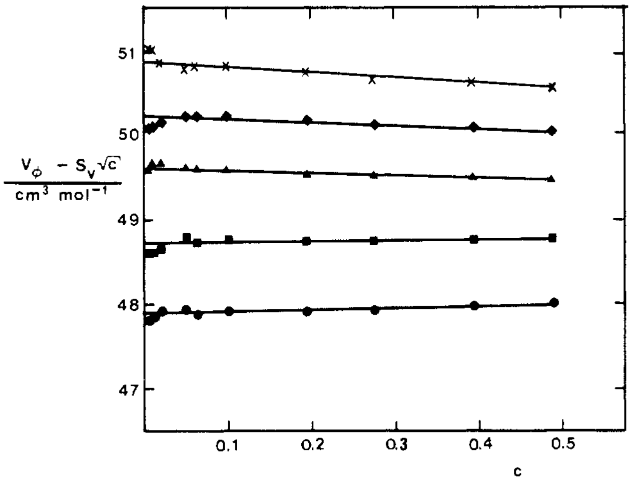

Figure 1. Apparent molal volumes plotted vs. concentration according to the Redlich equation, eq 1, at 15 (●), 20 (■), 25 (▲), 30 (◆), and 35 (×) °C.

pairs at the measured concentrations.

The partial molal volumes of KSCN at infinite dilution in Table II could be fitted to a parabolic function with respect to temperature with very high precision. The coefficient of determination turned out to be 0.999. It thus proved possible to calculate the partial molal expansibility, $E^0{}_2 = (\partial V^0{}_2/\partial T)$, with reasonable accuracy. The results are given in Table II.

The isentropic apparent molal compressibilities have also been calculated from the usual equations (*5*). By differentiating eq 1 with respect to pressure one can extrapolate the apparent molal compressibility to infinite dilution:

$$K_{\phi,s} = K_{\phi,s}{}^0 + S_K\sqrt{c} + b_K c \qquad (2)$$

In principle it is possible to calculate S_K from $\partial S_V/\partial P$, but the results rely upon the second derivative of the dielectric constant of water with respect to pressure ($\partial^2 \ln D/\partial P^2$). It was therefore considered more favorable to use empirically derived values of S_K from Sakurai et al. (*9*). The result has been plotted in Figure 2, and the infinite-dilution values and the deviation parameter are presented in Table III.

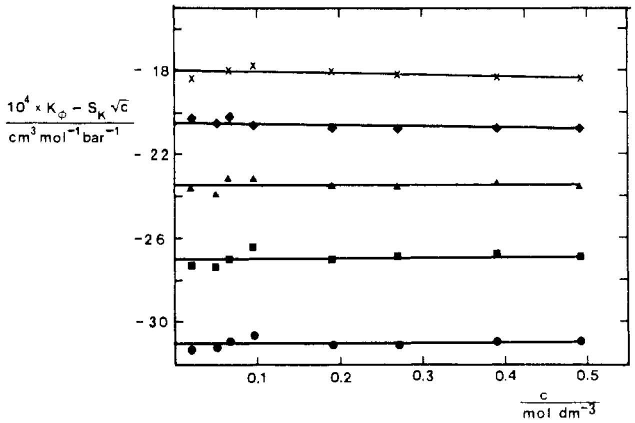

Figure 2. Isentropic apparent molal compressibilities vs. concentration according to eq 2. Symbols as in Figure 1.

Table III. Isentropic and Isothermal Partial Molal Compressibilities of KSCN in Aqueous Solution[a]

t, °C	$10^4K_{2,s}$,[b] cm^3 mol^{-1} bar^{-1}	$10^4b_{K,s}$, cm^3 mol^{-2} dm^3 bar^{-1}	$10^4K^0{}_2$,[c] cm^3 mol^{-1} bar^{-1}
15.0	−31.0	0.1	−27.0
20.0	−27.0	0.2	−22.1
25.0	−23.5	0.0	−18.0
30.0	−20.5	−0.6	−14.8
35.0	−18.0	−1.0	−12.4

[a] The deviation parameters from the limiting law for the isentropic values are also included. [b] ±0.2. [c] ±0.6.

Desnoyers and Philip (*10*) have derived a convenient equation for the conversion of isentropic partial molal compressibilities at infinite dilution to isothermal values:

$$K_\phi{}^0 = K_{\phi,s}{}^0 + \delta_0(2E^0{}_2/\alpha_0 - C_p{}^0{}_2/\sigma_0) \qquad (3)$$

Here $\delta_0 = \beta_0 - \beta_{0,s}$, the difference between the isothermal and isentropic compressibilities of water. The first can be taken from the data of Kell (*11*), and the isentropic value can be calculated from the speed of sound measurements of Del Grosso and Mader (*12*). $E^0{}_2$ is the partial molal expansibility of the solute at infinite dilution, α_0 the expansibility of water given by Kell (*11*), σ_0 the volumetric specific heat of water, and $C_p{}^0{}_2$ the partial molal heat capacity of the solute at infinite dilution. $C_p{}^0{}_2$ for KSCN at 25 °C is −18.4 J mol^{-1} K^{-1} (*13*). This means that the term $\delta_0 C_p{}^0{}_2/\delta_0$ is 2 × 10^{-6} cm^3 mol^{-1} bar^{-1} at 25 °C, which is far below the experimental error (±2 × 10^{-5}). It is thus not necessary to consider this term at 25 °C, and it is further assumed that it can be neglected at the other temperatures as well. (In fact, the absolute value of $C_p{}^\circ{}_2$ would have to increase more than 10 times with a temperature increase or decrease of 10 °C to make any sort of contribution.)

The isothermal partial molal compressibilities can thus be calculated as $K_{\phi,s}{}^0 + 2\delta_0(E^0{}_2/\alpha_0)$. The results are given in Table III.

Registry No. KSCN, 333-20-0.

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Solubility of Butane and Isobutane in Butanol, Chlorobenzene, and Carbon Tetrachloride

Claude Blais and Walter Hayduk*

Department of Chemical Engineering, University of Ottawa, Ottawa, Canada K1N 9B4

Solubilities of butane and isobutane gases are reported for the temperatures 298.15 and 323.15 K and atmospheric pressure for the solvents 1-butanol, chlorobenzene, and carbon tetrachloride. The solubilities were sufficiently high, in the range from 5 to 33 mol % gas in solution, so that special modifications were required for the accurate measurement of these solubilities. Butane was consistently more soluble than isobutane.

Introduction

The solubilities of butane and isobutane were measured in benzene and in normal paraffins from pentane to decane by Jadot (*1*) using a gas-chromatographic technique. Retention times in the chromatographic column were used to estimate Henry's constant at effectively very low gas partial pressures. Henry's constant was also measured by Jadot for butane in carbon tetrachloride so that a comparison with the solubility reported in this paper was possible. Some possible error is introduced when it is assumed that the same Henry's constant applies at atmospheric pressure.

Lenoir et al. (*2*) also utilized a chromatographic technique at low gas partial pressures for measuring the solubilities of butane and isobutane in several highly polar solvents. A more recent modification of the chromatographic technique was reported by Renon and co-workers (*3*) involving stripping of a gas-saturated solution. Solubilities of butane were reported by those workers in C_{16} paraffins. Solubilities of butane and isobutane were reported by Chappelow and Prausnitz (*4*) for high molecular weight solvents to relatively high temperatures using a combined volumetric and material-balanced method to determine Henry's law constants for approximately atmospheric pressure.

Solubilities of propane and butane had previously been measured in this laboratory by Castañeda (*5*) in several paraffin solvents from hexane to hexadecane and also in 1-butanol. The procedure used was similar to that utilized in this work.

For gases of high solubility such as butane and isobutane the normal boiling point temperature of the gas can be considered to be an extension of the solubility curve; that is, as the saturation temperature is reduced, the solution becomes richer in the gas until, at the gas normal boiling point, only the pure gas remains. Propane and butane have previously been shown to exhibit high solubilities at low temperature (*5*). It is expected, therefore, that the order of increasing solubility of a number of gases in a single solvent usually follows the order of increasing boiling point temperatures of the gases.

For nonpolar solvents, a linear extrapolation of all gas solubilities to the solvent critical temperature generally yields a common value or reference solubility. This phenomenon has been used as a basis for determining the temperature coefficient of solubility especially for gases in nonpolar solvents (*6*). Even for highly polar and associating solvents such as water, it was shown that the solubilities of many gases could also be extrapolated to a common solubility at the solvent critical temperature (*7*). Finally, it would appear that this type of extrapolation occurs with sufficient regularity that it may be used as a consistency test for solubility data involving nonpolar gases and liquids.

Experimental Section

The solubility method used in these experiments involved the continuous saturation of a constant flow of degassed solvent fed to the top of a glass absorption spiral by means of a calibrated syringe pump. The pressure in the absorption spiral was observed by means of a small monometer filled with saturated solution and located at the outlet of the spiral. Dry gas was confined in a gas buret over mercury while the pressure was kept constant by using a mercury-lift device driven by a variable-speed motor whose rate could be adjusted as required. The residence time of the solvent in the absorption spiral was approximately 15-30 min during which time saturation was complete. The solubility was determined from the constant solvent feed rate to the apparatus and the absorption rate of the dry gas. The linear relation between the two was confirmed by regular readings for at least 60 min of operation after steady-state conditions prevailed.

The solubility apparatus was similar to that used previously (*8*) but with appropriate modifications for accurate measure-

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