International Journal of the Physical Sciences Vol. 6(24), pp. 5716-5719, 16 October, 2011
Available online at http://www.academicjournals.org/IJPS
DOI: 10.5897/IJPS09.328
ISSN 1992 - 1950 ©2011 Academic Journals

Full Length Research Paper

Quantitative analysis of cohesive energy density: A Gordon parameter of 1:1 aqueous sodium salts solutions

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Accepted 14 April, 2011

The Gordon parameter ($\gamma/V_2^{1/2}$(dyne mol$^{1/2}$)/cm^2) of solutions of $NaNO_3$, NaCl and CH_3COONa binary mixtures of water in composition range 0.4 to 8.7, 0.6 to 4.6 and 0.4 to 6.1 mol/kg (m), respectively are reported. The cohesive energy density data are analyzed in terms of aggregation of the water molecules around ionic sphere. The 13 ((dyne mol$^{1/2}$)/cm^2) value of the Gordon parameter ($\gamma/V_2^{1/2}$) was noted for effective aggregation, but with CH_3COONa, the Gordon parameter ($\gamma/V_2^{1/2}$) and 0.6 to 2.8 m NaCl, the values were less than 13, whereas from 2.9 to 4.6 m NaCl, they were 2 times higher than 13. The dilute $NaNO_3$ solutions produced lower values and the concentrated solutions produced in manifold higher values than 13.

Key words: Cohesive energy, binary mixtures, molecular interactions, cohesive energy density, survismeter.

INTRODUCTION

The surface tension γ (dyne/cm) and apparent molar volumes or molar volume V_2 (cm^3/mol) data of $NaNO_3$, NaCl and CH_3COONa solutions were varied with increase in compositions and the solvent properties promote molecular interactions (Man and Ajay, 2006). Gordon parameter (Gordon, 1975) denoted as cohesive energy density ($\gamma/V_2^{1/2}$(dyne mol$^{1/2}$)/cm^2) directly related to polarity of the solvent and was calculated as shown in Equation 1:

$$\text{Gordon parameter} = \gamma/ V_2^{1/2} \quad (1)$$

Gordon (1975) proposed cohesive energy density ($\gamma/V^{1/2}$), a measure of solvent polarity, and incorporates the surface forces represented by γ and intermolecular forces represented by the V_2 molar volume. This matches to Hildebrand solubility parameter (John, 1984), but it is useful to study disruption of a lattice of the $NaNO_3$, NaCl and CH_3COONa salts on dissolution in water. The Hildebrand solubility parameter is the square root of the cohesive energy density. The cohesive energy density is an amount of energy needed to completely remove unit volume of molecules from their neighbors to infinite separation. In order for a material to dissolve, these same interactions need to be overcome as the molecules are separated from each other and surrounded by the solvent. Hildebrand suggested the square root of the cohesive energy density as a numerical value indicating solvency behavior known as the Hildebrand solubility parameter. The $NaNO_3$, NaCl and CH_3COONa with similar solubility parameters are noted to interact with water resulting in solvation.

EXPERIMENTAL PROCEDURE

The survismeter and pycnometer were the same as those reported elsewhere (Man and Ajay, 2006; Man, 2006) for surface tension and densities measurements, conducted at 30 ± 0.01°C. AnalaR grade NaCl, $NaNO_3$ and CH_3COONa (E. Merck, India) were dried at 110°C for 12 h before use, and stored in P_2O_5 filled desiccator at room temperature for 24 h. The dryness was checked with anhydrous $CuSO_4$ salt. The w/w, solutions were prepared with Millipore water of 4×10^{-6} S cm^{-1} conductivity. The densities of water were taken from literature (Man and Ajay, 2006). The surface tension γ of the solutions was calculated from Equation 2:

$$\gamma = [(n_0/n)\rho/\rho_0)]\gamma_0 \quad (2)$$

ρ is the density of the solution and ρ_0 is the density of the solvent in1x10^3 kg m^{-3}, t and t_0, the efflux time in sec and the γ_0, the solvent surface tension in 0.1 kg m^{-1}s^{-1}. An average uncertainty in surface

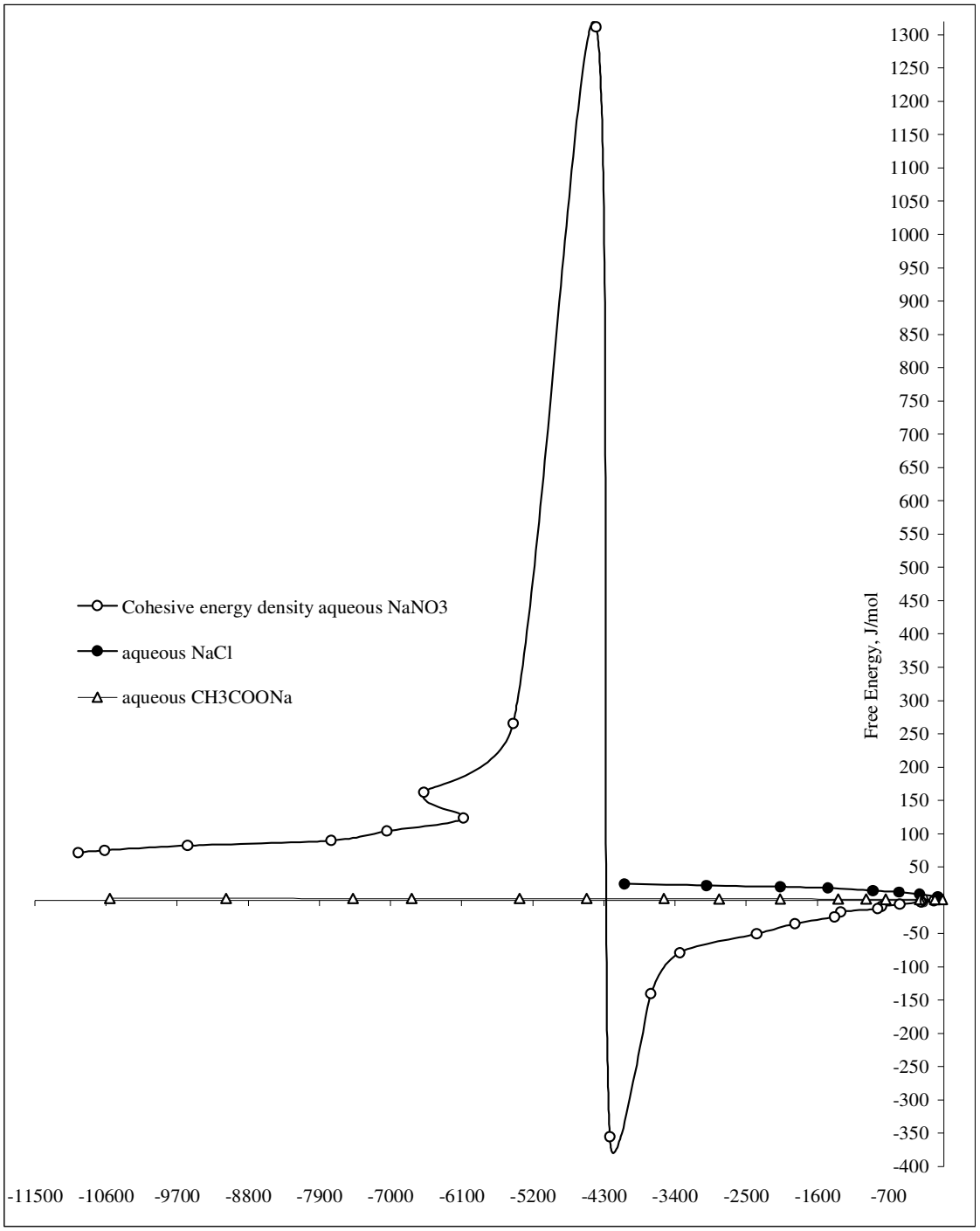

Figure 1. Gordon parameter y/V for 1:1 aqueous electrolyte salts solutions, cohesive energy density.

tension was noted less than 0.08%. The density 0.99565 × 10^3kg m^{-3} and surface tension 70.4 m/Nm of water at 30°C were used5. The V_2 molar volume was calculated from Equation 3

$$V_2 = 1/\rho[(M-(1000/m)(\rho-\rho_0)/\rho_0)] \quad (3)$$

The M molar mass and m mol kg^{-1}, errors in V_2 were calculated with $\pm V_2 = \Delta\rho(1000/m)$.

RESULTS AND DISCUSSION

The results of the Gordon parameter of salts solutions have been recorded in Table 1. This is displayed in Figure 1 where free energy of transfer of salts from solid to solvent water is plotted against γ/V_2 values. A linear relation in the values of the γ and γ/V_2 is noted for NaCl

Table 1. Molality (mmol/kg), density (1×10^3kg m^{-3}), V_2 molar volume (cm^3 mol^{-1}), γ surface tension (dyne/cm), ΔG free energy (J/mol) and Gordon parameter (γ/V_2).

m	Density	V_2	γ	ΔG	γ/V_2
$NaNo_3$					
0.4	1.08970	-142.08	77.05	-121.11	-1.08
0.8	1.11828	-63.80	76.99	-280.73	-2.41
0.8	1.11828	-63.80	76.99	-288.67	-2.41
1.6	1.17544	-25.19	78.85	-554.91	-6.26
2.0	1.20402	-17.66	80.77	-784.93	-9.15
2.4	1.23260	-12.74	80.62	-834.56	-12.66
2.8	1.26117	-9.30	82.49	-1303.35	-17.74
3.2	1.28975	-6.78	84.36	-1382.03	-24.88
3.5	1.31833	-4.87	86.22	-1881.43	-35.37
3.9	1.34691	-3.39	85.95	-2364.69	-50.64
4.3	1.37549	-2.22	87.77	-3337.51	-79.06
4.7	1.40407	-1.27	89.59	-3706.29	-140.60
5.1	1.43265	-0.50	89.24	-4222.84	-355.53
5.5	1.46123	0.14	88.90	-4397.21	1311.59
5.9	1.48981	0.67	88.58	-5446.03	265.78
6.3	1.51839	1.11	90.28	-6577.14	162.35
6.7	1.54697	1.49	91.98	-6076.94	123.60
7.1	1.57555	1.81	93.68	-7044.72	103.65
7.5	1.60413	2.08	93.26	-7750.57	89.68
7.9	1.63270	2.31	94.92	-9567.01	82.10
8.3	1.66128	2.51	94.48	-10617.37	75.23
8.7	1.68986	2.68	96.11	-10950.44	71.63
NaCl					
0.6	1.01365	26.55	70.42	-73.88	5.31
1.1	1.04394	15.44	68.89	-305.33	8.92
1.7	1.07423	11.66	69.73	-565.28	11.96
2.3	1.10453	9.72	70.54	-895.15	14.52
2.9	1.13482	8.51	77.47	-1465.13	18.22
3.4	1.16511	7.67	78.19	-2066.34	20.40
4.0	1.19540	7.04	77.60	-3001.74	22.03
4.6	1.22569	6.56	80.89	-4039.84	24.68
CH_3COONa					
0.4	0.94094	230.23	67.01	-15.00	0.58
0.8	0.95575	137.17	67.10	-114.83	0.98
1.2	0.97055	105.70	67.19	-302.22	1.27
1.6	0.98535	89.65	67.27	-734.20	1.50
2.0	1.00015	79.77	67.81	-982.85	1.70
2.4	1.01496	72.99	67.89	-1333.78	1.86
2.9	1.02976	67.99	67.96	-2067.78	2.00
3.3	1.04456	64.10	68.03	-2842.33	2.12
3.7	1.05937	60.96	68.10	-3536.86	2.23
4.1	1.07417	58.35	67.73	-4520.57	2.32

and CH_3COONa but $NaNO_3$ at around 6 m showed drastic rise and decrease in ΔG and cohesive energy density. This is due to transition of the $NaNO_3$ into the NO_3^- that develops a hydrated complex which also goes

under transition. A micellization decreases the cohesive energy density at around 6.8 m $NaNO_3$, thus the NO_3^- tends to develop micelles. So a driving force for aggregation decreases causing critical micelle concentration (CMC). Perhaps NO_3^- develops 3 D hydrated sphere structures. Gordon parameter explained water structure disruption and was reported less than 13 for aprotic solvents like dimethylsulfoxide (DMSO) but for $NaNO_3$ and NaCl, the Gordon parameter is 1311 and 24, and for CH_3COONa it is 2.5. The Gordon parameter is a measure of liquids cohesiveness and the liquids with Gordon parameter above 13 tend to promote aggregation of molecules. The Gordon parameters for NaNO3 around 5.6 to 7.98 m is more than 78 but from 7.8 to 8.6 m, it is lower than 78 (Figure 1).

For 0.57 to 2.8 m NaCl, the Gordon parameter is less than 13 but from 2.9 to 4.6 m, it is more than 13 and is almost 2 times higher. For 0.4 to 6.1 m CH_3COONa, the parameter is less than 13. The aprotic solvents like the DMOS possess high cohesive energy density, almost equal to 15 dyne $mol^{1/2}/cm^2$. The solvent of high dielectric constant (μ in Debye) like hydrazine, μ = 7.3 Debye, also promotes a molecular aggregation but the water with μ = 1.8 Debye promotes aggregation weakly. Thus the cohesive energy density for highly concentrated aqueous $NaNO_3$ is higher with comparatively more aggregation, but with the CH_3COONa due to CH_3 groups, the aggregates are formed and the NaCl develops moderate aggregate.

ACKNOWLEDGMENTS

The author is thankful to Dr. A. P. Raste, Principal, Deshbandhu College, University of Delhi, New Delhi.

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