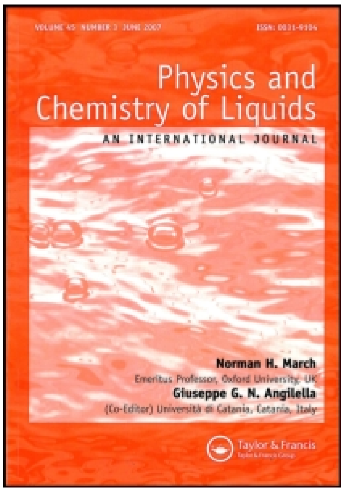

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Misra, P. K. and Chakravortty, V.(1996) 'Viscosity and Ultrasonic Studies of Carbonato-Bis (Ethylene Diamine) Cobalt(III) Perchlorate in Water and Glycerol-Water Mixed Solvent Systems', Physics and Chemistry of Liquids, 32: 1, 57 — 66

To link to this Article: DOI: 10.1080/00319109608030706

URL: http://dx.doi.org/10.1080/00319109608030706

Phys. Chem. Liq., 1996, Vol. 32, pp. 57–66
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VISCOSITY AND ULTRASONIC STUDIES OF CARBONATO-BIS (ETHYLENE DIAMINE) COBALT(III) PERCHLORATE IN WATER AND GLYCEROL-WATER MIXED SOLVENT SYSTEMS

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(Received 4 December 1995)

The ultrasonic velocity, density and viscosity of carbonato-bis(ethylene diamine) cobalt(III) perchlorate solution in water and 10%, 20%, 30%, 40% glycerol-water mixtures have been measured at 303.15 K. Various acoustic parameters such as isentropic compressibility, free length, acoustic impedance have been obtained from the experimental data for all the solutions. The nature of variation of these acoustic parameters give information about the type of interaction taking place in these systems. The co-ordination complex behaves as a structure breaker in glycerol-water mixed solvents.

KEY WORDS: Viscosity, acoustic parameters, solute-solvent interaction.

1. INTRODUCTION

Viscometry is one of the important tools for the determination of ion-solvent interactions which are the controlling forces in dilute solutions, where ion-ion interactions are negligible[1]. The variations of solvational properties are reflected in the viscosity *B*-coefficient values. Isentropic compressibility and apparent molal compressibility data, acoustic impedance, intermolecular freelength which are calculated from the measured ultrasonic velocity provide a lot of valuable information about the molecular environments and the nature of interactions. With this aim in view we report ultrasonic velocity, density and viscosity for solutions of carbonato-bis (ethylene diamine) cobalt(III) perchlorate in water and glycerol-water mixture (10%, 20%, 30% and 40%) at 303.15 K.

2. MATERIALS AND METHODS

Carbonato-bis(ethylene diamine) cobalt(III) perchlorate was prepared according to published method[2]. A. R. Grade (B.D.H) glycerol was used to prepare 10%, 20%,

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30%, and 40% (v/v) solutions in distilled water. The solutions were prepared on molar basis by dissolving known weights of the solute in appropriate volumes of the respective solvents and were kept for 2 h in a thermostat at 303.15 K. with an accuracy of 0.01 K. The experimental procedure followed for determination of density, viscosity and ultrasonic velocity was same as reported earlier[3]. The electrolyte content in the solution varied over a range of 0.001 to 0.01 M. Five observations were taken for each measurement and difference in any two readings did not exceed 0.02%.

3. THEORETICAL ASPECTS

The emperical equation of Jones and Dole[4]

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \tag{1}$$

relates the relative viscosity of an electrolytic solution to the concentration 'c' of the electrolyte. The constant A depends on the long range coulombic forces[5,6] and is of importance only in case of very dilute solutions. The parameter B which represents the ion-solvent interaction[7], has been interpreted as a measure of structure forming or structure breaking capacity of an electrolyte in solution[8]. The parameters A and B are determined from the intercept and slope of the linear plots of $(\eta/\eta_0 - 1)/c^{1/2}$ vs $c^{1/2}$. The B coefficients are related to the molar volumes of the electrolyte by

$$B = 2.5 \times \bar{V} \tag{2}$$

$\bar{V}$ represents the volume of the hole created by the electrolyte in the solvent system.

The apparent molal volume Φ_v was calculated from the density data by the standard procedure[8]. The limiting apparent molal volume Φ_v^0, was determined from the equation

$$\Phi_v = \Phi_v^o + S_v c^{1/2} \tag{3}$$

where S_v is the slope in the Φ_v versus $c^{1/2}$ plot and 'c' is the molarity.

From the ultrasonic velocity (U), isentropic compressibility (β_s), intermolecular freelength (L_f), molar sound velocity (R), acoustic impedance (Z), apparent molal compressibility (Φ_k), molar compressibility (W) and solvation number (S_n) are calculable[3] with the help of the following equations

$$\beta_s = U^{-2} \cdot \rho^{-1} \tag{4}$$

$$L_f = K \cdot \beta_s^{1/2} \tag{5}$$

$$R = U^{1/3} \cdot V_T \tag{6}$$

$$V_T = \bar{M} \rho^{-1} \tag{7}$$

$$\Phi_k = \frac{1000 \beta_s}{c} - \frac{\beta_s^0}{\rho_0} \left(\frac{1000, \rho}{c} - M \right) \tag{8}$$

$$Z = \rho \cdot U \tag{9}$$

$$W = \beta_s^{-1/2} \cdot V_T \tag{10}$$

$$S_n = \frac{n_1}{n_2} \left(1 - \frac{V \beta_s}{\eta_1 V_1^0 \beta_s^0} \right) \tag{11}$$

where ρ_0 and ρ are densities of the solvent and solution; M, molecular mass of the solute; β_s^0 and β_s, the isentropic compressibilities of solvent and solution; c, concentration in mol.dm^{-3}; K, temperature-dependent constant; $\bar{M}$, relative molecular mass; n_1 and n_2 are the number of moles of the solvent and solute respectively and V_1^0 is the molar volume of the solvent.

The values of β_s, calculated for solutions of different concentrations are found to obey Bachem's relationship[9],

$$\beta_s = \beta_s^0 + Cc + Dc^{3/2} \tag{12}$$

where C and D are constants and c is the concentration of the solution. The values of the constants C and D are obtained from the intercept and slope of the linear plots of $\beta_s - \beta_s^0/c$ vs $c^{1/2}$ respectively.

The limiting apparent molal compressibility, Φ_k^0, was obtained for a set of solutions of variable concentrations using the linear extrapolation of Φ_k vs $c^{1/2}$ according to the equation

$$\Phi_k = \Phi_k^0 + S_k c^{1/2} \tag{13}$$

where S_k is a constant.

The variation of solvation number with the molar concentration of the solute leads to a limiting solvation number S_n^0 which is evaluated through the relationship

$$\lim_{c \to 0} \Phi_k^0 = -S_n^0 V_1^0 \beta_s^0 \tag{14}$$

4. RESULTS AND DISCUSSION

Perusal of Table 1 reveals that Φ_v^0 values are positive indicating a strong solute-solvent interaction. It is dependent on the nature of the solute and structure of the

Table 1 Values of Φ_v^0, S_v, $\bar{V}$ and parameters A and B of the Jones-Dole equation for carbonato-bis (ethylene diamine) cobalt(III) perchlorate in different solutions at 303.15 K.

Solvent	Φ_v^0 $cm^3 mol^{-1}$	S_v $cm^{3/2}$ $mol^{-3/2}$	A $dm^{3/2} mol^{-1/2}$	B $dm^3 mol^{-1}$	$\bar{V}$ $dm^3 mol^{-1}$
Water	299.90	− 1420.70	0.14	1.16	0.46
10% glycerol	123.82	− 371.37	− 1.26	12.31	4.92
20% glycerol	96.00	4.17	− 1.52	12.17	4.87
30% glycerol	87.86	274.60	− 1.46	7.54	3.02
40% glycerol	77.60	386.00	− 0.52	6.96	2.78

solvent. Trend in variation of Φ_v^0 reflects that the solute-solvent interaction decreases with increasing glycerol content in the solvent. S_v may be considered as a measure of ion-ion interaction. Positive values of S_v in case of 20%, 30% and 40% glycerol show the interaction in increasing order.

The values of A (Tab. 1) are negative and hence have no physical significance[10]. However, very low value in case of water shows less ionic interaction. The B coefficient values (Fig. 1) suggest solute-solvent interaction. The values (Tab. 1) decrease with increasing glycerol concentration; indicating decrease in solute-solvent

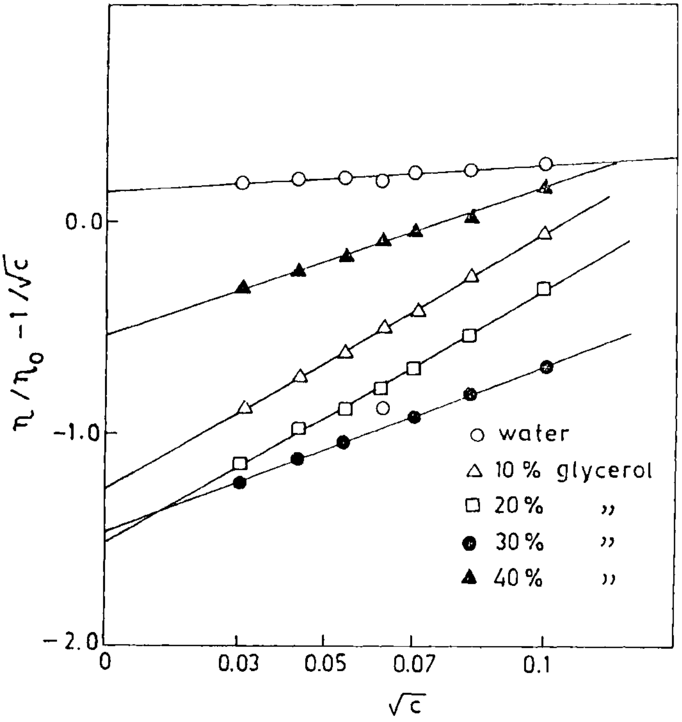

Figure 1 Plot of $\eta/\eta_0 - 1/\sqrt{c}$ vs $\sqrt{c}$ for carbonato-bis-(ethylene diamine) cobalt(III) perchlorate in water and glycerol-water mixture.

interaction. This fact corroborates our finding Φ_v^0. The decrease in B and $\bar{V}$ values with increase in glycerol content suggest that the complex $[Co(en)_2CO_3]ClO_4$ acts as a structure breaker.

A positive deviation in sound velocity (Fig. 2) and negative deviation in β_s values are observed with all the solutions in the concentration range studied. The variation in β_s values may be explained in terms of (i) dispersion forces and (ii) charge transfer, dipole-dipole and dipole induced dipole interactions. The former factor increases the intermolecular path lengths, as described by Jacobson[11]. This in turn causes negative deviation in sound velocity and positive deviation in compressibility. The latter factor, on the other hand, decreases the intermolecular path lengths leading to a positive deviation in sound velocity and negative deviation in compressibility. The actual values of β_s depend upon the relative strengths of the two opposing effects. The results of the present work indicate that the latter effect is dominant in all the systems which is corroborated by the decrease in L_f values (Fig. 4). The L_f values are comparatively higher in case of solutions with water than that in mixed solvents. This variation is probably due to higher internal pressure in water than that in

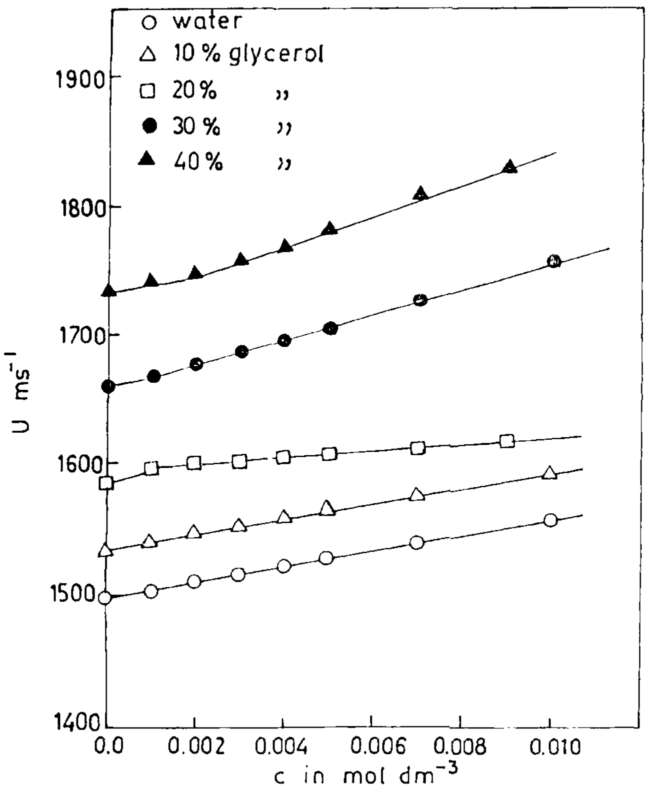

Figure 2 Variation of 'U' vs 'C' for carbonato-bis-(ethylene diamine) cobalt(III) perchlorate in water and glycerol-water mixture.

glycerol-water mixture. The variation of $(\beta_s - \beta_s^o)$ with concentration is plotted for each solution (Fig. 3). The values of constants C and D of the equation (12) are calculated by using least square method. It is observed that the C values are less negative with increasing glycerol content in the solvent; showing more solute-solute interaction. The D values are high and positive with water, 10%, and 20% glycerol, indicating presence of solute-solvent interaction in increasing order.

The limiting apparent molal compressibility (Φ_k^0) values are negative for all the solutions studied and decreases with increase in glycerol content, indicating poor compressibility of the solutions. The slope S_k of the equation (13) are positive up to 20% glycerol solution.

The molar sound velocity (R) increases with increase in concentration of the complex and with increase in glycerol percentage almost linearly (Fig. 5). This shows that the relative association in the solution increases with the increase in solute concentration. It is inferred that when the complex is added to the solvent, the association in the solvent increases due to increased solvation of the ions in the complex.

The molar compressibility (W) and acoustic impedance (Z), both increase with increase in concentration of the solutions in an almost linear manner (Figs. 6 and 7). The increasing order of 'Z' with concentration can be attributed as decreasing number of aggregates of solvent molecules with increase in concentration of the complex. Addition of more complex to the solvent leads to the acceleration of the process of breaking of aggregates of the solvent molecules.

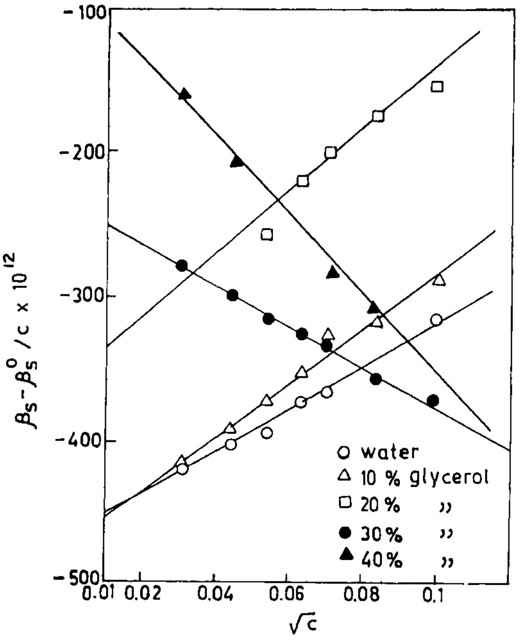

Figure 3 Variation of $(\beta_s - \beta_s^0)/c$ vs $\sqrt{c}$ for carbonato-bis-(ethylene diamine) cobalt(III) perchlorate in water and glycerol-water mixture.

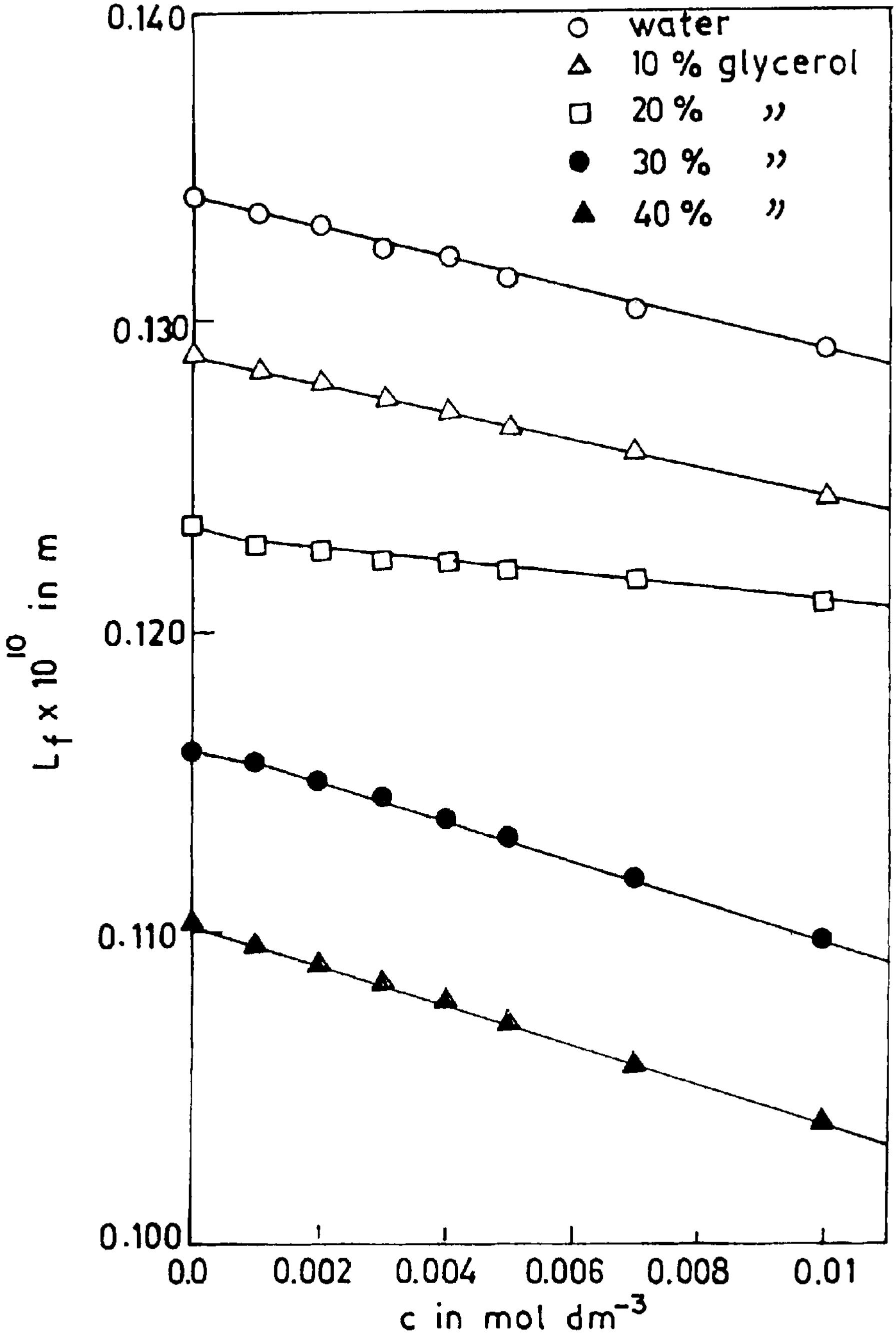

Figure 4 Variation of L_f vs. 'C' for carbonato-bis-(ethylene diamine) cobalt(III) perchlorate in water and glycerol-water mixture.

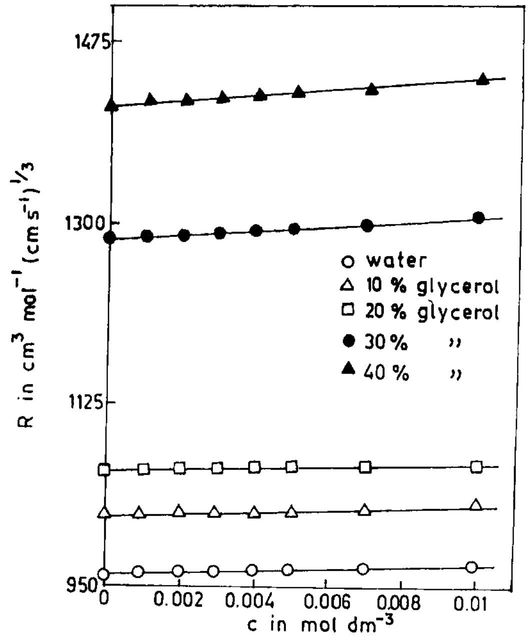

Figure 5 Variation of '*R*' vs '*C*' for carbonato-bis-(ethylene diamine) cobalt(III) perchlorate in water and glycerol-water mixture.

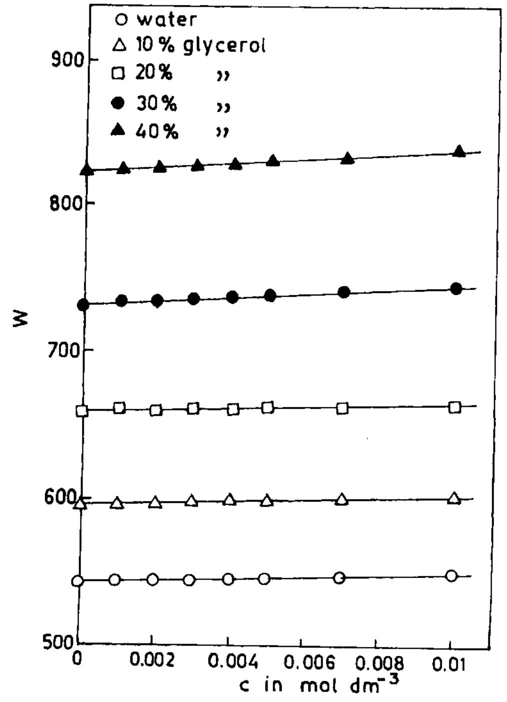

Figure 6 Variation of '*W*' vs. '*C*' for carbonato-bis-(ethylene diamine) cobalt(III) perchlorate in water and glycerol-water mixture.

The higher values of limiting solvation number S_n^0, (Tab. 2) in case of mixed solvents suggest that the solvation layer formed around the ions is thick and/or hard. The degree of electrostrictive solvation decreases with increasing glycerol content in the solution.

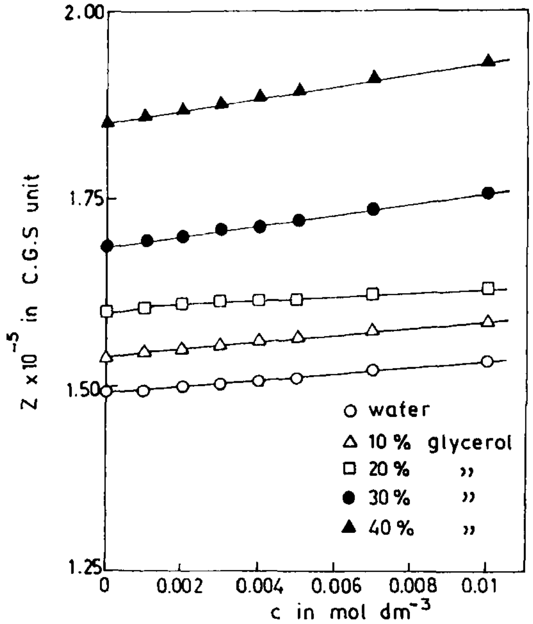

Figure 7 Variation of 'Z' vs 'C' for carbonato-bis-(ethylene diamine) cobalt(III) perchlorate in water and glycerol-water mixture.

Table 2 Values of constants C and D of Eqn. (12) along with Φ_k^o, S_k, and S_n^o in different solutions for carbonato-bis (ethylene diamine) cobalt(III) perchlorate at 303.15 K.

Solvent	$-C \times 10^{12}$	$D \times 10^{10}$	$-\Phi_k^o \times 10^9$	$S_k \times 10^7$	S_n^0
Water	473.32	15.41	462.47	15.23	569.23
10% glycerol	469.25	18.25	489.90	21.37	600.91
20% glycerol	461.22	36.28	477.16	36.18	610.81
30% glycerol	243.65	−12.58	245.71	−11.99	312.37
40% glycerol	117.28	−22.91	113.78	−22.92	145.71

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