

Evaluation of Ultrasonic Velocity in Binary Liquid Mixtures

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The experimental ultrasonic velocity of binary liquid mixtures is compared with theoretical values based on Nomoto's relation, Van Deal and Vangeel additive mixture relations. An attempt has been made to explain the positive as well as negative excess values obtained in three types of mixtures studied.

Key Words: Ultrasonic velocity, Binary liquid mixtures.

INTRODUCTION

The ultrasonic velocity of liquid mixtures is determined by different techniques. The velocity can also be evaluated theoretically using Nomoto's relation¹ and ideal mixture relation due to Van Deal². The validity of these two theoretical relations have been tested by number of authors³⁻⁷.

At present an attempt has been made to calculate theoretically the velocity of liquid mixtures, using Nomoto's and Van Deal's ideal mixture relations in order to compare the relative merits of the two relations. The percentage deviation of sound velocity from Nomoto's formula, Rao's constant, Wada's constant and molar volume were calculated. The molecular interaction,

$$\alpha = [(U_{\text{expt}}/U_{\text{im}})^2 - 1]$$

was also calculated. U_{expt} being experimental velocity and U_{im} referring to velocity due to ideal mixture relation. In order to work out the calculations, the experimental data were taken from the authors work.

Nomoto's relation

There is an empirical formula for the sound velocity in binary liquid mixtures consisting of two component liquids A and B. It was derived by Nomoto¹ on the assumption that there is a linear dependence of the molecular sound velocity $R = V \cdot U^{1/3}$ (V = molar volume and U = ultrasonic velocity) on concentration (the mole fractions of liquid A and B being X_1 and X_2) and the molar volume is additive.

The sound velocity of the mixture can be calculated by using the relation.

$$U = (R/V)^3 = [(X_1 R_A + X_2 R_B)/(X_1 V_A + X_2 V_B)]^3 \quad (1)$$

Van deal and Vongeel additive mixture relation

The relation suggested by Van Deal and Vongeel² for the sound velocity in homogeneous liquid mixtures is

$$\beta \frac{im}{s} = \phi_A (V_A / V^{im}) (\beta_s)_A + \phi_B (V_B / V^{im}) (\beta_s)_B \quad (2)$$

where the letters stand for usual notations.

The following expression for the sound velocity in mixture is given by

$$[1/(X_1 M_A + X_2 M_B)(U_{im}^2)] = [X_1 M_A U_A^2] + [X_2 M_B / U_B^2] \quad (3)$$

where M is the molecular weight.

The percentage deviations of the properties are given by the equation

$$[(A_{\text{expt}} - A_{\text{theo}})/A_{\text{expt}}] \%$$

where A represents the properties such as ultrasonic velocity (U), Rao's constant ($R = V \cdot U^{1/3}$), Wada's constant ($\beta = V \cdot \beta^{1/7}$) and molar volume ($V = M/\rho$). The A_{theo} is given by

$$A_{\text{theo}} = X_1 A_1 + X_2 A_2 \quad (4)$$

where A_1 and A_2 are the concerned properties of liquids 1 and 2, respectively.

The molecular interaction term α is given by

$$\alpha = [(U_{\text{expt}}/U_{\text{im}})^2 - 1]$$

EXPERIMENTAL

Component liquids were of AnalaR grade. Three binary mixtures of organic liquid were *o*-cresol acetophenone, *o*-cresol ethyl acetate and *o*-cresol methyl ethyl ketone prepared using various concentrations.

RESULTS AND DISCUSSION

For the liquid mixtures of *o*-cresol with acetophenone, ethyl acetate and methyl ethyl ketone, the ultrasonic velocities both experimental and theoretical, the percentage deviation of sound velocity from Nomoto's formula along with percentage deviation of Rao's constant, molar volume and molecular interaction term α are given in Table-1.

From Table-1, one can infer that the velocity values calculated by both Nomoto's relation, ideal mixtures relation closely follow the experimental velocity values in the case of *o*-cresol acetophenone mixture. In the case of *o*-cresol-ethyl acetate and *o*-cresol-methyl-ethyl ketone mixtures, the velocity values evaluated by Nomoto's relation shows better agreement with the experimental than the ideal mixture relation.

It also follows that *o*-cresol + acetophenone, *o*-cresol + ethyl acetate and *o*-cresol + methyl ethyl ketone mixtures show the maximum value of molecular interaction around 0.53, 0.69 and 0.47 mole fractions of *o*-cresol, respectively.

In the case of *o*-cresol-acetophenone, the percentage deviation of velocity due to Nomoto, Rao's constant, Wada's constant, molar volume and molecular interaction term α have not exceeded 0.48, 0.13, 0.1, 0.19 and 0.01, respectively. The percentage deviations of velocity and interaction deviations of Rao's constant, Wada's constant and molar volume are both positive and negative.

In the case of *o*-cresol-ethyl acetate mixture, the percentage deviation of velocity due to Nomoto, Rao' constant, Wada's constant and molar volume and molecular interaction term α have not exceeded 1.43, 1.61, 1.37, 1.92 and 1.1, respectively. The percentage deviations of velocity and interaction term α are found to positive only, where as the percentage deviations of Rao's constant, Wada's constant and molar volume are found to be negative.

In the case of *o*-cresol-methyl ethyl ketone mixture, the percentage deviation of velocity due to Nomoto, Rao's constant, Wada's constant, molar volume and molecular interaction term α have not exceeded 2.6, 0.6, 0.49, 1.26 and 0.21, respectively. The percentage deviations of velocity and molecular interaction term are found to be positive, that of molar volume negative and that of Rao's constant and Wada's constant both positive and negative.

Tiwari and Pandey⁸ in their ultrasonic investigation of benzene-tetrahydrofuran and methyl ethyl ketone-butanol mixtures describe as follows: The deviations from the ideal behaviour are generally attributed to the difference in size of the molecular and the strength of interaction between them. When negative excess functions are observed experimentally, more often complex formation is suspected. The occurrence of discrete groups of molecules arranged into specific geometric structures is suggested. These structural arrangements are influenced not only by the shape of the molecules but also by their mutual interactions. Consequently, the deviations from ideality in binary liquid mixtures provide a powerful means for the production of intermolecular interactions.

Fort and Moore⁹ have studied some 14 binary liquid mixtures and clearly established that the positive contributions for excess values should be attributed to dispersion forces and negative excess values should be due to charge transfer, dipole-induced dipole, dipole-dipole interaction. The positive as well as the negative excess values are found in all the three mixtures under study (Table-1). Hence, in the three types of mixtures, there is a possibility of dispersion forces, charge transfer, dipole-induced dipole and dipole-dipole interaction.

TABLE-1
THE ULTRASONIC VELOCITIES U BOTH EXPERIMENTAL & THEORETICAL, % DEVIATION OF U FROM NOMOTO'S RELATION,
% DEVIATION OF RAO'S CONSTANT, MOLAR VOLUME & MOLECULAR INTERACTION ' α ' AT DIFFERENT CONCENTRATIONS
OF LIQUID MIXTURES OF *o*-CRESOL WITH ACETOPHENONE, ETHYL ACETATE & METHYL ETHYL KETONE

m.f. of <i>o</i> -cresol (%)	Expt. U-m/s	Nomoto U-m/s	Ideal mixture U-m/s	($\Delta U/U$) %	$\Delta R/R$ %	($\Delta B/B$) %	($\Delta V/V$) %	α
<i>o</i> -cresol & Acetophenone								
0.00	1441	1441	1441	0.00	0.00	0.00	0.00	0.000
22.14	1453	1447	1448	+0.41	+0.13	+0.11	0.00	+0.007
32.77	1455	1451	1452	+0.27	+0.09	+0.07	0.00	+0.004
53.21	1467	1460	1459	+0.48	+0.08	+0.06	-0.09	+0.011
72.63	1471	1465	1467	+0.41	-0.06	-0.06	-0.19	+0.006
81.98	1473	1472	1471	+0.07	-0.07	-0.08	-0.09	+0.003
100.00	1478	1478	1478	0.00	0.00	0.00	0.00	0.000
<i>o</i> -cresol & Ethyl acetate								
0.00	1103	1103	1103	0.00	0.00	0.00	0.00	0.00
19.34	1182	1172	1142	+0.85	-0.17	-0.12	-0.50	+0.07
39.00	1262	1244	1192	+1.43	-0.41	-1.34	-0.90	+0.12
48.96	1293	1281	1223	+0.93	-1.61	-1.37	-1.92	+0.12
69.12	1364	1355	1300	+0.66	-0.72	-0.70	-0.99	+0.10
89.62	1438	1437	1407	+0.07	-0.19	-0.20	-0.19	+0.04
100.00	1478	1478	1478	0.00	0.00	0.00	0.00	0.00
<i>o</i> -cresol & Methyl ethyl Ketone								
0.00	1154	1154	1154	0.00	0.00	0.00	0.00	0.00
8.89	1187	1184	1160	+0.25	+0.60	-0.49	-0.66	+0.05
27.35	1272	1246	1183	+2.04	+0.20	-0.12	-0.86	+0.16
46.76	1344	1309	1222	+2.60	-0.35	-0.27	-1.26	+0.21
56.85	1366	1342	1251	+1.76	-0.47	-0.39	-1.03	+0.19
77.85	1424	1409	1335	+1.05	-0.12	-0.10	-0.50	+0.14
100.00	1478	1478	1478	0.00	0.00	0.00	0.00	0.00

*The number of significant figures is retained for internal consistency in calculations.

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