

Novel approach for prediction of ultrasonic velocity in quaternary liquid mixtures

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Abstract. A modified Flory theory along with the Auerbach and Altenberg relations has been employed for the computation of ultrasonic velocity of three quaternary liquid mixtures and a comparative study of all the three relations has then been carried out.

Keywords. Ultrasonic velocity; Flory theory; quaternary liquid mixture.

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1. Introduction

Present investigation makes an attempt to evaluate ultrasonic velocity of four quaternary liquid mixtures, in which for the first time, to the best of our knowledge, a modified Flory theory is being employed for the computation. An increasing interest in the study of intermolecular interactions coupled with an ever increasing demand for predictive equations for multicomponent systems form the basic aim of the present investigation. Significant amount of work has been carried out [1–4] in investigating liquid state properties by correlating ultrasonic velocity with numerous physical and thermodynamic parameters. The main reason for this being that sound velocity provides a very convenient and efficient pathway for determining several thermodynamical properties of liquid mixtures. Literature survey [5,6] reveals that previous workers have evaluated acoustical properties employing Flory theory in conjunction with empirical Auerbach [5] and Altenberg [5] relations for computation of quaternary and ternary liquid mixtures.

In the present study, the modified Flory theory along with Auerbach and Altenberg relations has been employed for the computation of ultrasonic velocity and a comparative study of all the three relations has then been carried out.

2. Theoretical

Ultrasonic velocity has been employed by modified Flory theory [7] using the expression

Table 1. Parameters for the pure components at 298.15 K.

Component	u (m s ⁻¹)	ρ (g cc ⁻³)	$\alpha \cdot 10^{-3}$ (K ⁻¹)	V (cc mol ⁻¹)	$\beta_T \cdot 10^{-11}$ (cm ² dyn ⁻¹)
<i>n</i> -Pentane	990	0.6216	1.6626	116.08	21.23
Toluene	1304	0.8627	1.0740	106.81	9.22
<i>n</i> -Heptane	1131	0.6791	1.2589	147.47	14.2
Cyclohexane	1253	0.7734	1.2150	108.76	11.4
<i>n</i> -Hexane	1076	0.6552	1.3897	131.53	17.1
Benzene	1296	0.8736	1.2265	89.82	9.67
<i>n</i> -Decane	1224	0.7263	1.0500	195.94	11.62

$$U_{\text{mix}} = \left(\frac{1}{\beta_{s,\text{mix}} \rho_{\text{mix}}} \right)^{1/2}, \quad (1)$$

where $\beta_{s,\text{mix}}$ and ρ_{mix} represent isentropic compressibility and density of the mixture. These parameters have been evaluated by Flory theory [3]. The Flory-Patterson theory [8] in conjunction with Auerbach relation gives the following expression for ultrasonic velocity:

$$U = \left(\frac{\sigma^* \tilde{\sigma}(\tilde{v})}{6.3 \times 10^{-4} \rho} \right)^{2/3}, \quad (2)$$

where

$$\sigma^* = K^{1/3} P^{*2/3} T^{*1/3} \quad (3)$$

and

$$\tilde{\sigma}(\tilde{v}) = M \tilde{v}^{-5/3} - \left(\frac{\tilde{v}^{1/3} - 1}{\tilde{v}^2} \ln \frac{\tilde{v}^{1/3} - 0.5}{\tilde{v}^{1/3} - 1} \right), \quad (4)$$

where all the notations have their usual significance and can be evaluated by the method proposed elsewhere [9].

Flory theory in conjunction with Altenberg's relation gives the following expression for evaluating ultrasonic velocity:

$$U = 5.663 \left(\frac{K^2 P^{*4} T^{*2} L}{\rho^2 M} \right)^{1/6} \times \left[M \tilde{v}^{-5/3} - \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^2} \ln \left\{ \frac{\tilde{v}^{1/3} - 0.5}{\tilde{v}^{1/3} - 1} \right\} \right], \quad (5)$$

where L is the Loschmidt number equal to 2.6872×10^{19} cm³ and P^* , \tilde{v} and T^* for the quaternary liquid mixtures have been computed by the method given elsewhere [6].

Ultrasonic velocity in quaternary liquid mixtures

Table 2. Ultrasonic velocity of quaternary systems by Flory theory, Auerbach and Altenberg relations at 298.15 K.

x_1	x_2	x_3	u (exp) (m s ⁻¹)	u (Flory) (m s ⁻¹)	u (Auerbach) (m s ⁻¹)	u (Altenberg) (m s ⁻¹)	% dev. Flory	% dev. Auerbach	% dev. Altenberg
<i>n</i> -Pentane+toluene+ <i>n</i> -heptane+cyclohexane									
0.0404	0.6358	0.1544	1270.10	1266.38	1317.40	1206.00	0.29	-3.72	5.05
0.0560	0.5737	0.1284	1256.30	1241.01	1314.20	1199.90	1.22	-4.61	4.49
0.0735	0.5474	0.1120	1243.50	1236.17	1310.60	1194.00	0.59	-5.40	3.98
0.0935	0.5282	0.0959	1230.20	1231.65	1308.10	1188.40	-0.12	-6.33	3.40
0.1141	0.5054	0.0793	1223.70	1226.56	1305.20	1181.80	-0.23	-6.66	3.42
0.1134	0.4948	0.0660	1232.30	1226.26	1308.30	1184.90	0.49	-6.17	3.85
0.1511	0.4602	0.0487	1218.70	1216.75	1299.70	1170.60	0.16	-6.65	3.95
0.1709	0.4395	0.0338	1213.20	1211.72	1294.70	1163.80	0.12	-6.72	4.07
0.1071	0.4099	0.0783	1234.50	1216.79	1304.30	1175.40	1.43	-5.65	4.79
0.1126	0.4267	0.1137	1218.10	1215.60	1301.20	1167.80	0.21	-6.82	4.13
0.1783	0.2174	0.1637	1201.50	1178.43	1286.20	1118.10	1.92	-7.05	6.94
0.1991	0.2200	0.1674	1199.20	1174.81	1283.30	1111.40	2.03	-7.01	7.32
0.1794	0.6020	0.1481	1233.20	1223.86	1293.70	1156.10	0.76	-4.91	6.25
0.1351	0.1100	0.1484	1217.20	1176.16	1291.20	1125.30	3.37	-6.08	7.55
0.0948	0.3338	0.2524	1227.50	1200.52	1301.30	1141.80	2.20	-6.01	6.98
						APD	0.96	-5.99	5.08
<i>n</i> -Pentane+ <i>n</i> -hexane+benzene+toluene									
0.0943	0.0918	0.4587	1260.10	1226.19	1292.70	1204.30	2.69	-2.59	4.43
0.1300	0.1373	0.2974	1233.20	1202.54	1285.20	1171.20	2.49	-4.22	5.03
0.1278	0.1288	0.3589	1237.30	1206.79	1282.70	1173.90	2.47	-3.67	5.12
0.1492	0.1384	0.3421	1217.90	1199.19	1278.20	1160.20	1.54	-4.95	4.74
0.1843	0.1484	0.2711	1200.10	1186.65	1273.50	1141.60	1.12	-6.12	4.87
0.1823	0.1640	0.3613	1197.90	1187.00	1267.10	1134.70	0.91	-5.78	5.28
0.1819	0.1601	0.3342	1200.10	1186.98	1269.30	1137.30	1.09	-5.77	5.23
0.1250	0.1655	0.2455	1223.10	1196.78	1282.30	1162.00	2.15	-4.84	5.00
0.1691	0.2041	0.2218	1201.30	1178.61	1271.40	1129.00	1.89	-5.84	6.02
0.1866	0.0826	0.1250	1229.30	1193.75	1286.90	1255.00	2.89	-4.69	-2.09
0.1372	0.1578	0.5548	1211.40	1206.31	1273.60	1256.00	0.42	-5.13	-3.68
0.0660	0.1053	0.7033	1268.10	1242.44	1287.30	1209.80	2.02	-1.51	4.60
0.0524	0.1434	0.4201	1260.50	1224.70	1298.20	1205.70	2.84	-2.99	4.35
0.1568	0.0468	0.4582	1256.30	1219.66	1283.40	1290.70	2.92	-2.16	-2.74
						APD	1.83	4.32	4.53
<i>n</i> -Pentane+ <i>n</i> -hexane+cyclohexane+benzene									
0.0488	0.1238	0.1831	1240.10	1206.55	1290.70	1193.90	2.71	-4.08	3.73
0.0658	0.1078	0.2036	1239.90	1205.61	1291.80	1190.90	2.77	-4.19	3.95
0.0813	0.0934	0.2238	1237.20	1204.76	1289.80	1186.80	2.62	-4.25	4.07
0.1006	0.0778	0.2430	1236.60	1203.24	1284.20	1180.60	2.70	-3.85	4.53
0.1180	0.0629	0.2615	1230.20	1202.06	1285.70	1177.00	2.29	-4.51	4.32
0.1243	0.0456	0.2842	1240.10	1203.96	1290.30	1180.30	2.91	-4.05	4.82
0.1410	0.1304	0.3129	1205.40	1185.44	1273.40	1136.00	1.66	-5.64	5.76
0.1560	0.1262	0.1513	1213.50	1181.01	1268.30	1143.00	2.68	-4.52	5.81
0.1285	0.1192	0.5888	1206.20	1193.07	1278.80	1123.00	1.09	-6.02	6.90
0.1537	0.0925	0.1685	1226.40	1187.54	1271.10	1155.00	3.17	-3.64	5.82
0.1649	0.1013	0.5177	1194.30	1187.37	1274.90	1119.70	0.58	-6.75	6.25
0.1368	0.1258	0.1507	1210.50	1185.41	1274.50	1153.50	2.07	-5.29	4.71
0.0910	0.1721	0.6137	1201.60	1192.26	1280.20	1119.00	0.78	-6.54	6.87
0.0649	0.1378	0.1103	1263.70	1199.54	1234.80	1186.50	5.08	2.29	6.11
0.1810	0.1656	0.2970	1197.40	1170.37	1264.70	1108.10	2.26	-5.62	7.46
						APD	2.36	4.44	5.41

3. Results and discussion

A modified Flory theory along with Auerbach and Altenberg relations in conjunction with Flory theory have been employed to compute the ultrasonic velocity of three quaternary liquid mixtures viz., *n*-pentane + toluene + *n*-heptane +

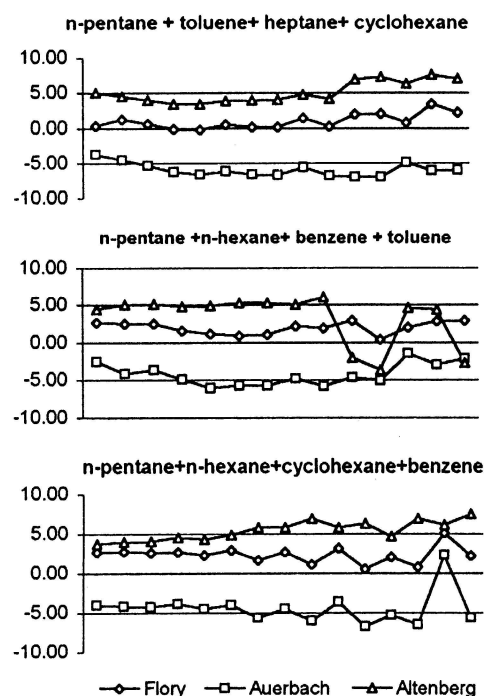


Figure 1. Average percentage deviations for the quaternary systems by Flory, Auerbach and Altenberg relations at 298.15 K.

cyclohexane, *n*-pentane + *n*-hexane + benzene + toluene and *n*-pentane + *n*-hexane + cyclohexane + benzene at 298.15 K. The modified Flory theory has been put to test since it is for the first time that the modified form is being used to predict the ultrasonic velocity of quaternary liquid mixtures. An assessment has then been made on the merits of the three approaches. Table 1 records the necessary data for the pure components, which have been taken from literature [5]. Table 2 lists the values of the experimental ultrasonic velocity taken from literature [5], theoretically computed values of ultrasonic velocity using Flory relation, Auerbach and Altenberg relations along with their average percentage deviations at 298.15 K, using eqs (1), (2) and (5). Figures 1a–c provide a graphical representation of the average percentage deviations of the three quaternary systems under investigation with respect to the experimental values as computed by the three methods viz., Flory, Auerbach and Altenberg relations respectively at 298.15 K.

A perusal of table 2 reveals that the modified Flory theory performs admirably as compared to the other two relations, for all the systems under consideration as the average percentage deviation (APD) values of the three systems follow the order: Flory < Altenberg < Auerbach (System I) and Flory < Auerbach < Altenberg (Systems II and III).

The above observation makes the validity of the Flory theory for the prediction of the three systems under investigation all the more significant. Also evident is the fact that both Auerbach and Altenberg relations, which employ surface tension

values for computation of ultrasonic velocity, show deviations between 4 and 6%, in spite of the limitations of both the relations, since none of the components of the quaternary liquid mixture strictly obey the theorem of corresponding states, which forms the basis of extension of theory for computation of surface tension.

Further, only two-body interactions have been accounted for whereas there definitely exists possibilities of higher order interactions and this fact is validated when these relations, on being applied to ternary systems, give better results due to decrease in the number of possible interactions. Another factor, which proves to be a drawback for these two methods, is the application of the reduced surface tension of the mixture by considering it to consist of an equivalent single component, which is not very feasible. Such a consideration does not take into account the concentration of the components at the surface of the mixture.

Thus we conclude by saying that the modified Flory theory, which employs the thermal expansion coefficient (α) and isothermal compressibility (β_T) values of ultrasonic velocity, definitely shows superiority over the remaining two methods. The results can show a definite improvement if one has access to experimental data of α , β_T and heat capacity at constant pressure, C_p , data, as will be seen in our forthcoming investigation.

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