SHORT COMMUNICATIONS

EVALUATION OF SOUND VELOCITY AND INTERACTION STUDIES IN BINARY LIQUID MIXTURES

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ATTEMPTS have been made earlier[1,2] to evaluate sound velocity assuming linearity of molar sound velocity. Sound velocity in liquid mixtures was evaluated[3] on the basis of additivity of the adiabatic compressibility. The interaction in binary liquid mixtures from a knowledge of the excess thermodynamic functions and some acoustical parameters was also extensively studied[4–9].

In the present communication sound velocity has been evaluated in binary liquid mixtures butyl amine + cyclohexane and butyl amine + methyl cyclohexane using the aforesaid methods, and the result has been compared with experimental findings. Molar sound velocity (R) and molar compressibility (W) have also been evaluated for the title binaries. The present investigation also aims at studying the interaction in terms of $U^2_{\text{exp}}/U^2_{\text{im}}$, since the deviation of the term from unity is a direct measure of nonideality.

Nomoto derived an empirical formula for the sound velocity (U) assuming the linearity of the molar sound velocity, namely

$$R = x_1 R_1 + x_2 R_2, \qquad (1)$$

where R_1 and R_2 are the molar sound velocioty of the component 1 and 2 whose molefractions are x_1 and x_2 respectively. The molar sound velocity R, also known as Rao's constant[10] is related to sound velocity (U) by the relation

$$R = \frac{M}{\rho} U^{1/3} = V U^{1/3}, \qquad (2)$$

where ρ is the density, hence

$$U = (R/V)^3 = \left\{ \frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right\}^3 \qquad (3)$$

The molar compressibility (W) is related to adiaba-

tic compressibility (β_s) by the relation as given by Wada[11]

$$W = V_m \beta_s^{-1/7}, \qquad (4)$$

where,

$$\beta_s = U^{-2} \rho^{-1}. \qquad (5)$$

According to Van Dael's assumption the adiabatic compressibility (β_s) of the mixture is given by

$$\beta_{s(\text{im})} = \phi_1 \frac{\gamma_1}{\gamma_{\text{im}}} \beta_{s(1)} + \phi_2 \frac{\gamma_2}{\gamma_{\text{im}}} \beta_{s(2)}, \qquad (6)$$

where ϕ and γ represent volume fraction and specific heat ratio respectively. To avoid complication a simple relation for $\beta_{s(\text{im})}$ is assumed as[12,13]

$$\beta_{s(\text{im})} = \phi_1 \beta_{s(1)} + \phi_2 \beta_{s(2)}. \qquad (7)$$

This is true only if the mixture is an ideal one and the condition $\gamma_1 = \gamma_2 = \gamma_{\text{im}}$ is satisfied. Equation (7) can be transformed into a linear combination of the molefraction by assuming $V_1 = V_2$.

$$\beta_{s(\text{im})} = x_1 \beta_{s(1)} + x_2 \beta_{s(2)}. \qquad (8)$$

In the light of (7) and (8) one gets the expression for sound velocity of the mixture as

$$\frac{1}{x_1 M_1 + x_2 M_2} \cdot \frac{1}{U^2_{\text{im}}} = \frac{x_1}{M_1 U_1^2} + \frac{x_2}{M_2 U_2^2}, \qquad (9)$$

where M_1, M_2, U_1, U_2 and x_1, x_2 are the molecular weight, sound velocity and molefraction of components 1 and 2 respectively, and U_{im} is the sound velocity of the binary liquid mixture by ideal mixing relation.

The sound velocity evaluated from Nomoto's relation and from ideal mixing relation is listed in table 1. The sound velocity and necessary data required for calculation have been taken from literature[14,15]. The experimental sound velocity is also given for comparison. An examination of table 1 reveals that there is an excellent agreement between theoretical and experimental sound velocity. The mean percentage deviation for butyl amine + cyclohexane and butyl amine + methyl cyclohexane are 1.66 and 1.46 by Nomoto's relation and 1.54 and 1.03 by ideal mixing relation respectively. The greater deviation in both the mixtures by

Table 1 *Sound velocity (U), molar sound velocity (R) and molar compressibility (W) for binary liquid mixtures at 30°C*

x_1^*	R_{mix}	W_{mix}	U_{exp} (m s^{-1})	U (N) (m sec^{-1})	U (V) (m sec^{-1})
Butyl amine + cyclohexane					
0.1147	1158.8	794.8	1216	1229.2	1228.3
0.2162	1148.0	786.7	1210	1230.3	1229.4
0.4064	1129.6	773.2	1206	1232.6	1230.3
0.5206	1119.3	765.4	1208	1233.9	1231.5
0.6270	1108.4	757.4	1210	1235.2	1233.0
0.7130	1099.8	751.1	1213	1236.3	1234.2
0.8120	1089.6	774.0	1218	1237.5	1236.1
0.9052	1081.0	737.2	1228	1238.6	1238.7
Butyl amine + methyl cyclohexane					
0.1352	1328.2	910.7	1188	1197.1	1193.8
0.2442	1295.5	887.5'	1186	1201.4	1196.3
0.3588	1260.6	863.2	1186	1206.3	1199.8
0.4439	1234.8	845.5	1188	1210.1	1203.2
0.5632	1199.0	820.0	1193	1215.8	1208.8
0.6594	1170.1	801.0	1198	1220.6	1214.2
0.7381	1146.8	783.3	1204	1224.7	1219.2
0.8425	1116.3	761.7	1214	1230.5	1226.7
0.9189	1094.7	746.4	1225	1235.0	1232.8

x_1^* represents molefraction of butyl amine.

Nomoto's relation may perhaps be due to non-inclusion of the excess volume V^L in the molar volume of the mixture. Actually the molar volume should be $x_1 V_1 + x_2 V_2 + V^E$ in (3). Molar sound velocity and molar compressibility have also been included in table 1. It is evident from the table that molar sound velocity and molar compressibility increase with increasing number of carbon atoms. In both the systems studied R and W decrease with increase in the concentration of butyl amine.

Variation of the ratio U_{exp}^2/U_{im}^2 with molefraction is shown in figure 1. The deviation of U_{exp}^2/U_{im}^2 from unity is a direct measure of the product (v/v^{im}). (γ/γ^{im}). (β_T^{im}/β_T), where V^{im}, γ^{im} and β_T^{im} are the molar volume, specific heat ratio and isothermal compressibility of an ideal mixture respectively (the isothermal compressibility (β_T) is related to adiabatic compressibility (β_s) and the specific heat ratio (γ) as $\beta_T = \gamma \cdot \beta_s$). Thus U_{exp}^2/U_{im}^2 can be used as an important tool to measure the nonideality in the mixture. An inspection of figure 1 shows that deviation of U_{exp}^2/U_{im}^2 from unity is negative for both the mixtures. The maximum deviation for butyl
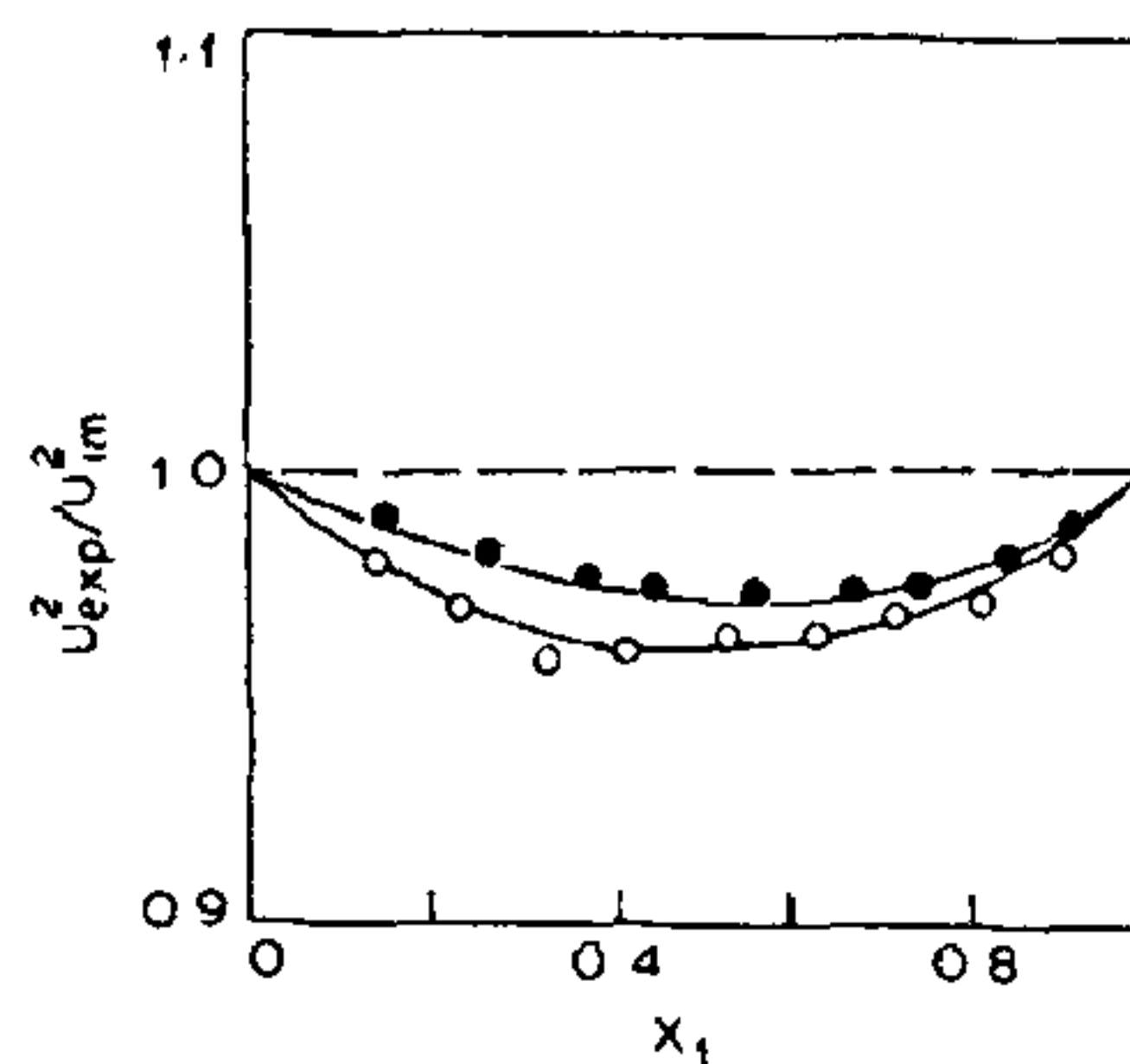
Figure 1. U_{exp}^2/U_{im}^2 versus (X_1) molefraction of butyl amine. o, butyl amine + cyclohexane; ●, butyl amine + methylcyclohexane.

amine + cyclohexane occurs in the vicinity of $x_1 = 0.3$ and for butyl amine + methyl cyclohexane is in the vicinity of $x_1 = 0.5$. The figure reveals that there is weak interaction in both the systems. However, the interaction decreases in butyl amine + methyl cyclohexane which may be due to steric hindrance of CH_3 group in methyl cyclohexane, a fact which has already been established[14,16].

From the above discussion it may be concluded that nonideality in binary liquid mixtures is capable of being expressed in terms of U_{exp}^2/U_{im}^2. Ideal mixing relation shows better agreement with experimental values, hence, it is to be preferred.
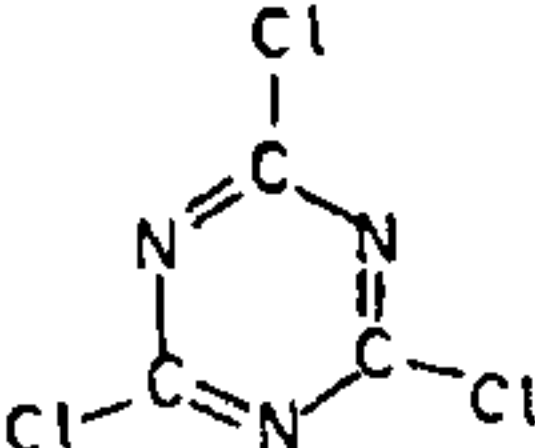
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Table 1 *P–Toluene sulphones 3 from reagent 1 and alkyl halides 2*

Alkyl halide 2	Reaction time (hr)	Yield (%)	M. P. (°C)
CH_3-I	6	98	89
CH_3-CH_2-I	7	90	56
CH_3-CH_2-CH_2-I	6	95	51
CH_2 = CH-CH_2-Br	2	89	54
C_6H_5-CH_2-Cl	5	99	92
C_6H_5-CO-CH_2-Br	2	98	108
p-Br-C_6H_4-CO-CH_2-Br	2	95	105
C_2H_5O-CO-CH_2-Cl	10	94	90
CH_3-CO-CH_2-Cl	5	90	74
	10	92	78

POLYMER SUPPORTED REAGENTS: AN IMPROVED SYNTHESIS OF SULPHONES USING ANION EXCHANGE RESINS

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SULPHONES are important drug intermediates[1] and are generally prepared either by oxidation of the corresponding sulphides or by a displacement reaction using sodium sulphinates as the nucleophile. A drawback of the former method is that the foul smelling thiols are the basic starting materials while the sulphinate method requires rather long reaction times and usually results only in moderate yields of sulphones[2,3].

Recently the procedure has been modified by using tetrabutylammonium-*p*-toluenesulphinate in the nucleophilic displacement reaction with organic halides[4] which gives satisfactory yields. However, the preparation of tetrabutylammonium-*p*-toluenesulphinate from sodium-*p*-toluenesulphinate and tetrabutylammonium bromide was not effective, since a two-fold excess of sodium-*p*-toluenesulphinate was required and the reagent effectively used in
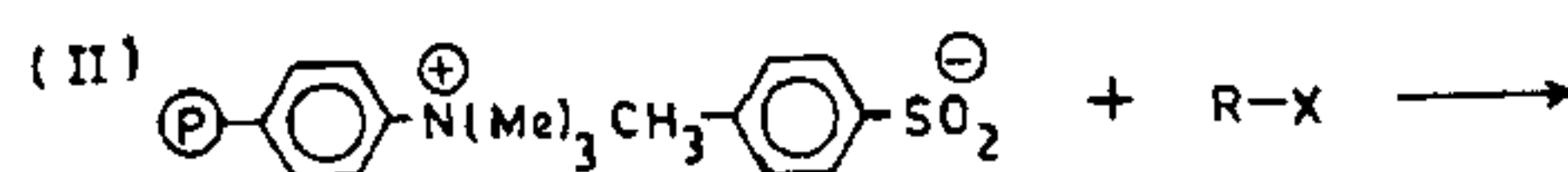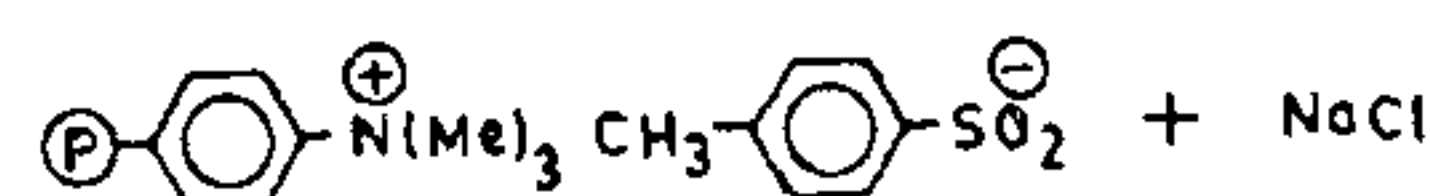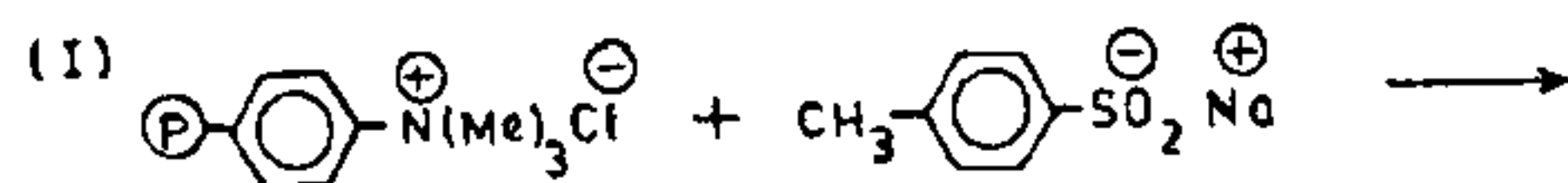
the alkylation reaction was only 50% pure.

As part of our work to demonstrate the applicability of polymer supported reagents in organic synthesis[5-7] we now report a more convenient method for the synthesis of sulphones by alkylation of *p*-toluenesulphinate anion supported on IRA 400, a strong anion exchange resin containing the quaternary ammonium group. The products obtained in high yields were essentially pure and characterized by their NMR, IR and comparison with authentic samples.

A typical procedure for the preparation of Amberlite IRA 400 *p*-toluenesulphinate: A 0.25 molar aqueous solution of the sodium salt of *p*-toluenesulphinic acid was slowly percolated through a column filled with Amberlite IRA 400 in chloride form, until a negative test for chloride ion in the eluate was obtained. The resin was then