sat	pure saturated liquid
∞	at infinite dilution
20	value at 20 °C

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Ultrasonic Velocities, Densities, and Viscosities of Triethylamine in Methanol, Ethanol, and 1-Propanol

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Ultrasonic velocities, densities, and viscosities of triethylamine in methanol, ethanol, and 1-propanol have been measured at 25 °C. From experimental data isentropic compressibility, molar volume, and their excess values along with excess viscosity and excess molar Gibbs free energy for the activation of flow have been computed and presented as functions of composition. The parameter *d* of the Grunberg and Nissan expression has also been calculated. The results indicate A-B-type interaction which decreases in strength with an increase in the chain length of alcohols.

Introduction

Considerable interest has been stimulated by the ultrasonic and viscosity investigations of binary liquid mixtures. The nonideal behavior of liquid mixtures has been predicted by Tuomikoski and Nurmi (*1*), Fort and Moore (*2*, *3*), Flory and coworkers (*4*, *5*), Prakash et al. (*6*), Nigam and Singh (*7*), and Raman and Naidu (*8*). The deviations from the law of additivity in the values of various parameters indicate the existence of specific interaction between unlike molecules. Triethylamine (TEA) is a weakly polar liquid, whereas alcohols are polar and associating. The present work deals with the study of ultrasonic velocity, isentropic compressibility, molar volume, viscosity, and excess values along with excess molar Gibbs free energy for activation of flow and the Grunberg and Nissan (*9*) term *d* for the systems (I) triethylamine (TEA)-methanol, (II) TEA-ethanol, and (III) TEA-1-propanol at 25 °C.

Experimental Section

Ultrasonic velocity at 2 MHz was measured by a single-crystal variable-path interferometer. The transducer was a gold-plated quartz cyrstal. The accuracy of velocity measurement was ±0.18%.

Density was determined by a double-walled pycnometer having capillaries of narrow bore provided with well-fitted glass caps in order to avoid changes in composition due to evaporation of the more volatile liquid. The accuracy in density is of the order of 0.03%. (See Table I.)

Table I. Densities of Chemicals

compd	density at 25 °C exptl	lit.	ref
triethylamine	0.7255	0.7254	*16*
methanol	0.7868	0.7870	*3*
ethanol	0.7851	0.78506	*17*
propanol	0.7996	0.79968	*18*

The suspended level Ostwald viscometer calibrated with benzene and double-distilled water was used for determining the viscosities. The values are accurate to 0.001 cP. The temperature was maintained constant by a thermostatic bath.

Ethanol (BCPW) and TEA, methanol, and 1-propanol (all BDH AR grade) were purified by Copp and Findlay's method (*10*). The mixtures were prepared by mixing weighed amounts of pure liquids and left for 2 h.

The isentropic compressibility β_s is given by

$$\beta_s = v^{-2}\rho - 1 \qquad (1)$$

where *v* is the ultrasonic velocity and ρ is the density. The molar volume *V* of a mixture is defined as

$$V = \bar{M}/\rho \qquad (2)$$

where $\bar{M} = xM_1 + (1 - x)M_2$, M_1 and *x* being the molecular weight and the mole fraction of the first component, respectively, and M_2 and $(1 - x)$ the molecular weight and the mole fraction of the second component, respectively. The viscosity was determined from eq 3, where *t* and η represent the time

$$\nu = \text{kinematic viscosity} = \eta/\rho = at - b/t \qquad (3)$$

of flow in seconds and the viscosity in centipoise, respectively, of the mixtures, whereas *a* and *b* are the constants of the

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Table II. Values of the Coefficient for Eq 9 Determined by the Method of Least Squares

system	function	a_0	a_1	a_2	σ
TEA-methanol	β_s^E	−42.11	25.9	−11.76	1.87
	V^E	−9.78	−0.26	1.12	0.08
	η^E	−0.006	−0.33	0.31	0.01
	G^E	359	−499	513	22
TEA–ethanol	β_s^E	−23.3	12.5	−102.7	2.24
	V^E	−8.5	4.4	2.1	0.08
	η^E	−0.67	0.2	1.3	0.03
	G^E	−18	−98	637	8.5
TEA-1-propanol	β_s^E	19.12	15.57	8.75	0.45
	V^E	−6.04	4.5	0.5	0.07
	η^E	−1.4	0.3	−0.2	0.02
	G^E	−188	−241	−204	42.7

viscometer. The excess values β_s^E, V^E, and η^E have been computed from eq 4–6. x is the mole fraction of TEA; subscripts 1 and 2 refer to components 1 and 2.

$$\beta_s^E = (\beta_s)_{mix} - [x\beta_{s_1} + (1 - x)\beta_{s_2}] \tag{4}$$

$$V^E = (V)_{mix} - [xV_1 + (1 - x)V_2] \tag{5}$$

$$\eta^E = (\eta)_{mix} - [x\eta_1 + (1 - x)\eta_2] \tag{6}$$

Grunberg and Nissan (*9*) formulated the following expression to define the interaction:

$$\ln \eta = x \ln \eta_1 + (1 - x) \ln \eta_2 + x(1 - x)d \tag{7}$$

d is a constant proportional to w, where w is the "interchange energy" (*11*) arising from the fact that, although the molecules of the two components of a regular solution are interchangeable as far as size and shape are concerned, there is an increase in the lattice energy when a molecule of component 1 is introduced into the lattice of component 2. Katti and Chaudhari (*12*) developed eq 8 for nonideal solutions. W_{vis} is an empirical parameter that represents (*13*) excess molar Gibbs free energy for activation of flow, G^E, which can be calculated from eq 9.

$$\ln \eta V = x \ln \eta_1 V_1 + (1 - x) \ln \eta_2 V_2 + x(1 - x)W_{vis}/(RT) \tag{8}$$

$$G^E = RT[\ln \eta V - x \ln \eta_1 V_1 - (1 - x) \ln \eta_2 V_2] \tag{9}$$

Each set of the results was fitted with a Redlich–Kister formula of the type in eq 10, where A^E represents the excess properties under consideration, a_j is the polynomial coefficient, and n is the polynomial degree. The least-squares method was used to determine the values of the coefficient a_j. In each case the optimum number of coefficients was ascertained from an examination of the variation of the standard error σ of the estimate with n (eq 11). The values for the coefficient a_j and the estimate of standard error have been given in Table II.

$$A^E = x(1 - x) \sum_{j=1}^{n} a_{j-1}[x - (1 - x)]^{j-1} \tag{10}$$

$$\sigma = [\sum(A^E_{obsd} - A^E_{calcd})^2/(n_{obsd} - n)]^{1/2} \tag{11}$$

Results

The experimental values of ultrasonic velocity (v), density (ρ), viscosity (η), isentropic compressibility (β_s) and parameter d have been given in Table III. The smooth value of excess isentropic compressibility (β_s^E), the excess molar volume (V^E), the excess viscosity (η^E), and the excess molar Gibbs free energy for the activation of flow (G^E) were computed by eq 10 using coefficients a_0, a_1, and a_2 and are presented in Figures 1–4.

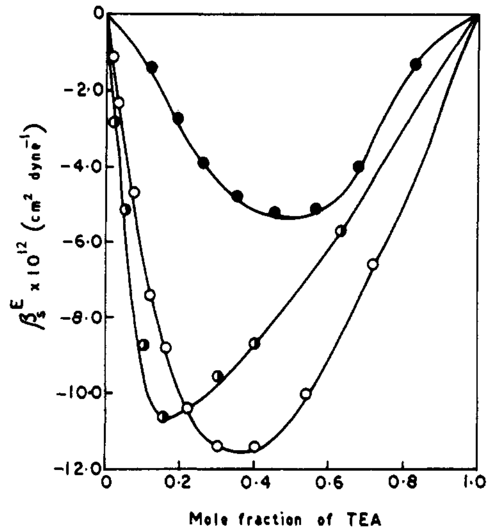


Figure 1. Excess isentropic compressibility vs. mole fraction of TEA in (○) TEA–methanol, (◐) TEA–ethanol, and (●) TEA-1-propanol at 25 °C.

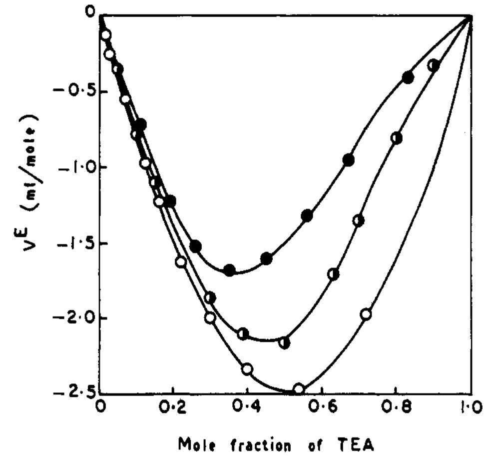


Figure 2. Excess molar volume vs. mole fraction of TEA in (○) TEA–methanol, (◐) TEA–ethanol, and (●) TEA-1-propanol at 25 °C.

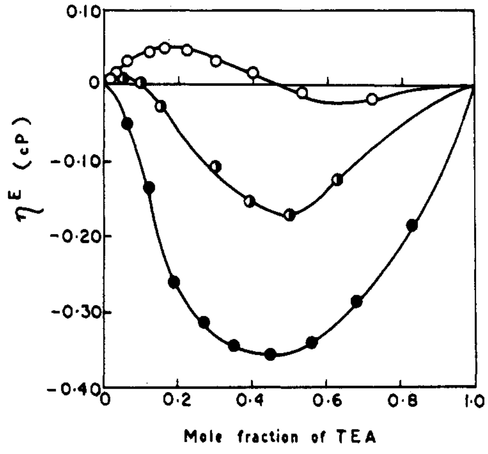


Figure 3. Excess viscosity vs. mole fraction of TEA in (○) TEA–methanol, (◐) TEA–ethanol, and (●) TEA-1-propanol at 25 °C.

Discussion

Ultrasonic velocity values are found to increase with the increasing mole fraction of TEA. As more and more TEA is added to alcohols, the velocity shows a downward trend. The viscosity in TEA–methanol increases at first, but it decreases

Table III. Ultrasonic Velocity, Density, Viscosity, Isentropic Compressibility, and Parameter d at 25 °C

x^a	$10^3 \nu$, m s^{-1}	ρ, g mL^{-1}	η, cP	β_s, cm^2 dyn^{-1}	d
		TEA–Methanol			
0	1.112	0.7868	0.5444	102.8	0
0.015	1.115	0.7862	0.5485	102.3	0.9
0.031	1.121	0.7855	0.5511	101.3	0.8
0.067	1.144	0.7834	0.5556	97.5	0.7
0.124	1.163	0.7815	0.5747	94.6	1.0
0.162	1.173	0.7803	0.5700	92.1	0.8
0.225	1.189	0.7778	0.5532	90.9	0.6
0.303	1.182	0.7727	0.5450	92.6	0.6
0.403	1.178	0.7658	0.5030	94.1	0.4
0.537	1.155	0.7565	0.4458	99.1	0.1
0.723	1.153	0.7438	0.4006	101.1	−0.001
1	1.120	0.7255	0.3563	109.9	0
		TEA–Ethanol			
0	1.160	0.7851	1.1347	94.6	0
0.022	1.181	0.7850	1.1240	91.3	0.7
0.045	1.189	0.7847	1.1131	90.1	0.8
0.095	1.194	0.7844	1.0707	89.4	0.6
0.153	1.196	0.7832	0.9630	89.2	0.1
0.296	1.194	0.7745	0.8051	90.6	0.0
0.387	1.188	0.7674	0.6842	92.3	−0.2
0.495	1.175	0.7592	0.5982	95.4	−0.2
0.627	1.165	0.7496	0.5113	98.3	−0.3
1	1.120	0.7255	0.3563	109.9	0
		TEA–1-Propanol			
0	1.213	0.7996	1.7618	84.9	0
0.118	1.216	0.7943	1.4405	85.1	−0.1
0.187	1.218	0.7903	1.2464	85.3	−0.3
0.264	1.214	0.7835	1.0992	86.6	−0.2
0.349	1.202	0.7755	0.9323	89.2	−0.3
0.446	1.196	0.7661	0.7394	91.2	−0.6
0.556	1.182	0.7573	0.6610	94.5	−0.4
0.682	1.164	0.7464	0.5021	98.9	−0.7
0.828	1.138	0.7353	0.4183	105.0	−0.8
1	1.120	0.7255	0.3563	109.9	0

[a] x = mole fraction of triethylamine.

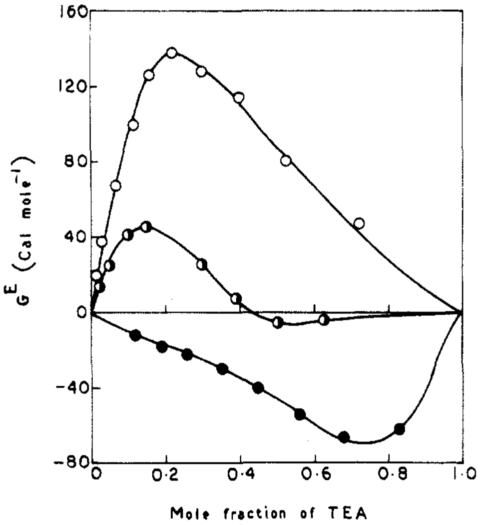
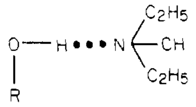


Figure 4. G^E vs. mole fraction of TEA in (○) TEA–methanol, (◑) TEA–ethanol, and (●) TEA–1-propanol at 25 °C.

when the mixture becomes rich in TEA. In the other two systems it decreases with increasing mole fraction of TEA. The parameter d of eq 7 is positive in TEA–methanol except when the mixture is very rich in TEA, when it is found to be negative. In TEA–ethanol d changes sign from positive to negative with increasing TEA content, but in TEA–1-propanol d is negative at all compositions.

Interestingly, V^E is negative in all three systems and at all compositions. Values of the excess volume may be attributed to (I) hydrogen-bond interaction between the unlike molecules leading to contraction in the volumes of alcohol mixtures as compared to the ideal mixtures and (II) breakup of the alcohol polymers on the addition of TEA, which contributes to the increase in the volume of alcohol mixtures. The observed values of V^E indicate that the association between unlike molecules predominates over dissociation of alcohol aggregates.

It has been reported (*2*) that β_s^E becomes increasingly negative as the strength of the interaction increases. β_s^E has been found to be negative in all three systems, but it becomes increasingly negative as we move from 1-propanol to ethanol and from ethanol to methanol. This suggests somewhat stronger interaction of TEA with methanol than with ethanol and 1-propanol. A similar conclusion can be drawn from the values of η^E which are negative for TEA–1-propanol. In TEA–ethanol η^E is negative in mixtures rich in TEA but becomes positive when the mole fraction of ethanol is higher. In the case of TEA–methanol, η^E is positive at all compositions except at 0.7227 mole fraction of TEA. G^E is positive in TEA–methanol and negative in TEA–1-propanol and changes from positive to negative in TEA–ethanol. According to Fort and Moore (*3*) and Ramamoorthy (*14*, *15*), systems exhibit strong interaction if the parameter d is positive; if it is negative they show weak interaction. On this basis also we can say that the interaction is stronger in TEA–methanol than in the other two systems. The results suggest A–B-type interaction forming



The strength of bonding is expected to decrease with the increase in chain length of the alcohols, and the results of this study corroborate this fact.

Glossary

v	ultrasonic velocity, m s^{-1}
β_s	isentropic compressibility, cm^2 dyn^{-1}
ρ	density, g mL^{-1}
σ	standard error
η	viscosity, cP
G	molar Gibbs free energy of activation of flow, cal mol^{-1}
V	molar volume, mL mol^{-1}
d	Grunberg and Nissan parameter
R	gas constant
t	time of flow, s
T	temperature, K
a	polynomial coefficient
n	polynominal degree

Subscripts

E	excess function
obsd	observed value
calcd	calculated value

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Selective Solvent Extraction of Trioxane from Formaldehyde Solution

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Two solvents, namely, dichlorobenzene and benzene, have been studied for extraction of 1,3,5-trioxane from formaldehyde solution. The ternary liquid equilibrium diagrams are presented for the systems trioxane–formaldehyde solution–solvents, at 50 and 60 °C. The tie line data matched well with the Othmer–Tobias correlation. Dichlorobenzene has been found to be the more selective solvent; it has less affinity for formaldehyde solution in the extract phase. The separation of trioxane and dichlorobenzene by distillation is also easier.

Trioxane is produced from formaldehyde, usually from its concentrated aqueous solution, by distillation in the presence of acid. The overhead stream thus obtained contains trioxane, water, and formaldehyde. Trioxane is recovered from this aqueous formaldehyde solution by extraction with a water-immiscible solvent. The extent of water and other organic impurities in the extracted trioxane depends mainly on the solvent and the operating conditions. Such impurities, even in traces, affect the polymer yield (*1*).

Little work has been published on the separation of trioxane from formaldehyde solution. Most of the literature data deal with its crystallization directly from the aqueous phase (*2–5*), or extraction by methylene chloride (*6–10*). Slivkin et al. (*11*) used benzene, toluene, and *o*-xylene as solvents at 50 °C and reported benzene as the best solvent if the trioxane is to be separated from the extract by rectification and toluene as the best if trioxane is to be crystallized from the extract. These studies were mainly based on the estimation of solubility and equilibrium relationships. The amounts of impurities of water and formaldehyde were, however, not considered in detail. The Meissner process (*12*) for trioxane production mentioned the use of monochloro-, dichloro-, or trichlorobenzene as solvent. They preferred the use of dichlorobenzene because of lower heat requirements and ease of separation of trioxane from the solvent by rectification. Selectivity and equilibrium data for these solvents were, however, not reported.

The present paper is concerned with the studies on the extraction of trioxane using benzene and dichlorobenzene as solvents at 50 and 60 °C. The phase-equilibrium relationships were determined, and the selectivities of the solvents as well as the solvent recovery data were examined for a general comparison.

Chemicals

The feed used was a mixture of pure trioxane, prepared in the laboratory, and aqueous formaldehyde solution in desired proportions. The solvents were of laboratory grade and were further purified by fractionation. For benzene, the fraction boiling at 80 °C and, for dichlorobenzene, the 172–179 °C fraction were collected and used.

Experimental Procedure

The solubilities of trioxane in the pure solvents and in the formaldehyde solution were determined in the conventional way, by finding out the temperatures of complete dissolution while varying the amounts of trioxane. The solubility of water in dichlorobenzene at different temperatures was determined by mixing the two liquids, maintaining the temperatures constant, and analyzing the solvent phase by Karl Fischer reagent.

The data for the phase equilibrium were collected in a conventional mixer–settler, consisting of a jacketed cylindrical glass vessel (75 mm i.d., 230 mm long) of 1-L capacity. It was provided with a two-bladed paddle agitator and a thermometer pocket. The speed of the agitator could be varied up to 800 rpm. The content of the mixer–settler was maintained at the desired temperature (±1 °C) by circulating oil through the jacket from a thermostatic bath. A measured amount (by weight) of the synthetic feed, containing trioxane in 25% formaldehyde solution, was first taken in the mixer–settler. A measured amount of solvent was then added and stirred for 1 h while maintaining constant temperature. The ratio of solvent to feed was varied from 1 to 5 in the different series of runs. After mixing, the contents were allowed to settle for 1 h. These periods were sufficient since preliminary experiments had shown that the phase equilibrium was established within 15 min of stirring and 0.5-h settling time was sufficient for phase separation.

The extract and the raffinate phases were separated and analyzed by GLC (*13*). Water contents in the extract phase were also determined by the Karl Fischer method. The benzene or the dichlorobenzene contents in the aqueous phase were analyzed by ultraviolet spectroscopy.

Results and Discussion

The system consisted of four components—water, formaldehyde, trioxane, and the solvent. But because of the high affinity of formaldehyde for water, the system appears to behave like a ternary system with formaldehyde and water together as a single component. This was confirmed by the observations that there was practically no difference in the solubility of trioxane in water and in 30% formaldehyde solution at various temperatures and that no phase separation occurred between formaldehyde and water (Figure 1). The solubilities of trioxane in benzene and dichlorobenzene were much higher than in the aqueous formaldehyde.

It is desirable that the water content in the trioxane product should be minimal since water affects the behavior of trioxane