ative in $NaClO_4$ systems and positive (at low concentrations) in CF_3COONa systems. Probably the first observation may be related to the $Na^+ \leftrightarrow C_3H_4O_3$ interaction, and the second one to the $CF_3 \leftrightarrow CF_3$ interaction.

The value of $\Delta T/m$ extrapolated to $m = 0$ is 7.8 K mol^{-1} kg ($NaClO_4$ solute) and 6.0 K mol^{-1} kg (CF_3COONa solute). The second value is less reliable owing to the shape of the curve. The melting point given in this note does not agree with the value reported in the literature (*16*); this difference may be a consequence of different purity of the sample employed. From the values T/K = 309.4 and K_{cr} = 7.8 K mol^{-1} kg, ΔH = 9.0 kJ/mol is obtained. Important supercooling phenomena were not observed: only without agitation the mixture with CF_3COONa supercools as much as 10 K in the concentration range, $X(CF_3COONa) \cong 0.45$.

Registry No. CF_3COONa, 2923-18-4; $NaClO_4$, 7601-89-0; $KClO_4$, 7778-74-7; 1,3-dioxolan-2-one, 96-49-1.

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Shear Viscosities of Binary Mixtures of Acrylonitrile + Cyclohexane, Benzene, *p*-Xylene, and Mesitylene at 307.4 K

R. R. Yadava* and S. S. Yadava[†]
Chemistry Department, Gorakhpur University, Gorakhpur 273 009, India

Viscosities of binary mixtures of acrylonitrile and nonpolar solvents (viz., cyclohexane, benzene, *p*-xylene, and mesitylene) have been measured at 307.4 K. The mixture viscosities show a marked negative deviation when the mixture is prepared with cyclohexane. However, this deviation has been found to gradually reduce in the case of benzene, *p*-xylene, and mesitylene. The parameter *d* has been calculated from the viscosity data and has been found to be a minimum (most negative value) in the case of cyclohexane. It increases gradually for benzene, *p*-xylene, and mesitylene. The values of interchange energy (W_{visc}) have also been calculated and have been found to show the opposite trend to that shown by the parameter *d*, i.e., most positive with cyclohexane, less positive with benzene, and negative and more negative with *p*-xylene and mesitylene, respectively.

Introduction

Various attempts have been made to correlate the extent of deviation of viscosity from its rectilinear dependence on the mole fractions and the values of the parameter *d* with the type and the degree of molecular interactions (*1-4*). The molecular interactions between acrylonitrile and some nonpolar aromatics have been already studied in our earlier papers (*5, 6*) by estimation of the dipole moments and it has been suggested that the complex formation is governed by dipole-induced dipole electrostatic attractions.

In order to confirm the earlier conclusion and to establish the suitability of the viscosity measurements for the study of such systems, it has been felt necessary to employ viscosity measurements for the system already studied by dielectric constant measurements.

Experimental Section

The binary systems studied were acrylonitrile + cyclohexane, acrylonitrile + benzene, acrylonitrile + *p*-xylene, and acrylonitrile + mesitylene. Acrylonitrile (B.D.H., L.R.), cyclohexane (B.D.H., L.R.), benzene (spectroscopic grade), and *p*-xylene and mesitylene (E. Merck) were used. All the chemicals, except that of spectroscopic grade, were purified before use and their purity was checked by density measurements.

The dynamic viscosities (η), of the liquids and liquid mixtures were measured at 307.4 ± 0.01 K as described elsewhere (*7*). The values of the viscosity were accurate within 0.01%. The densities of the liquids and liquid mixtures were measured pycnometrically. Precautions were taken to avoid losses due to evaporation. The density values were correct to ±0.000 1 g mL^{-1}.

Values of the parameter *d* for each sample of all the mixtures were calculated by eq 1, first suggested by Grunberg and

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \qquad (1)$$

Nissan (*8*), where η_1, η_2 and x_1, x_2 are the viscosities and mole fractions respectively of the components 1 and 2. η_{12} is the viscosity of the liquid mixture. The parameter *d* is proportional

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[†] Present address: Chemistry Department, Garhwal University Campus, Pauri (Garhwal), India.

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Table I. Mole Fraction of Acrylonitrile (X_2), Viscosity (η), d, and W_{visc} Values at 307.4 for the Acrylonitrile-Cyclohexane System

X_2	η, cP	ρ, g mL^{-1}	d	W_{visc}, kcal mol^{-1}
0.0000	0.760	0.7647		
0.0861	0.660	0.7630	−0.81	1.94
0.2848	0.530	0.7653	−0.51	1.12
0.5332	0.419	0.7672	−0.46	0.91
0.5440	0.396	0.7682	−0.65	1.27
0.7114	0.359	0.7723	−0.54	0.97
0.8989	0.318	0.7824	−0.69	1.16
1.0000	0.309	0.7871		

Table II. Mole Fraction of Acrylonitrile (X_2), Viscosity (η), d, and W_{visc} Values at 307.4 K for the Acrylonitrile-Benzene System

X_2	η, cP	ρ, g mL^{-1}	d	W_{visc}, kcal mol^{-1}
0.0000	0.530	0.8631		
0.0966	0.494	0.8585	−0.21	0.51
0.2512	0.448	0.8495	−0.17	0.41
0.4788	0.395	0.8339	−0.14	0.32
0.5188	0.386	0.8311	−0.15	0.33
0.6633	0.357	0.8197	−0.17	0.35
0.8844	0.320	0.8005	−0.27	0.54
1.0000	0.309	0.7871		

Table III. Mole Fraction of Acrylonitrile (X_2), Viscosity (η), d, and W_{visc} Values at 307.4 K for the Acrylonitrile-p-Xylene System

X_2	η, cP	ρ, g mL^{-1}	d	W_{visc}, kcal mol^{-1}
0.0000	0.539	0.8486		
0.1092	0.510	0.8450	0.06	0.14
0.3082	0.469	0.8389	0.15	−0.39
0.5430	0.414	0.8277	0.15	−0.41
0.6189	0.394	0.8230	0.13	−0.35
0.7270	0.368	0.8152	0.12	−0.31
0.9097	0.329	0.8020	0.15	−0.42
1.0000	0.309	0.7871		

Table IV. Mole Fraction of Acrylonitrile (X_2), Viscosity (η), d, and W_{visc} Values at 307.4 K for the Acrylonitrile-Mesitylene System

X_2	η, cP	ρ, g mL^{-1}	d	W_{visc}, kcal mol^{-1}
0.0000	0.584	0.8529		
0.1210	0.551	0.8498	0.18	−0.47
0.3367	0.495	0.8409	0.22	−0.60
0.5736	0.424	0.8277	0.19	−0.56
0.6490	0.406	0.8233	0.22	−0.65
0.7535	0.373	0.8148	0.17	−0.52
0.9118	0.332	0.7997	0.19	−0.63
1.0000	0.309	0.7871		

to the W/RT in the two-suffix Margules equation (1), W being the interchange energy. The viscosity data were processed to obtain the value of interchange energy (W_{visc}) by using the following equation

$$W_{visc} = \frac{RT \ln (\eta_{12}/\eta_1)}{A_1 x_1 x_2 \left[x_2 + \frac{A_2}{A_1} x_1 \right]}$$

where the various terms carry their usual significance (*1*).

Results and Discussion

The values of the viscosity (η), the parameter d, and the interchange energy (W_{visc}) as a function of composition for all the systems studied are reported in Tables I–IV. The variation of viscosities of the liquid mixtures with the mole fractions of acrylonitrile for all the systems studied is graphically represented in Figures 1–4.

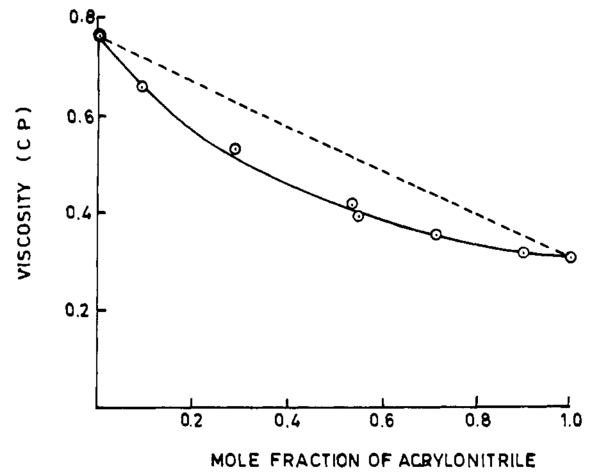

Figure 1. Variation of viscosity at 307.4 K with mole fraction of acrylonitrile in acrylonitrile-cyclohexane mixture.

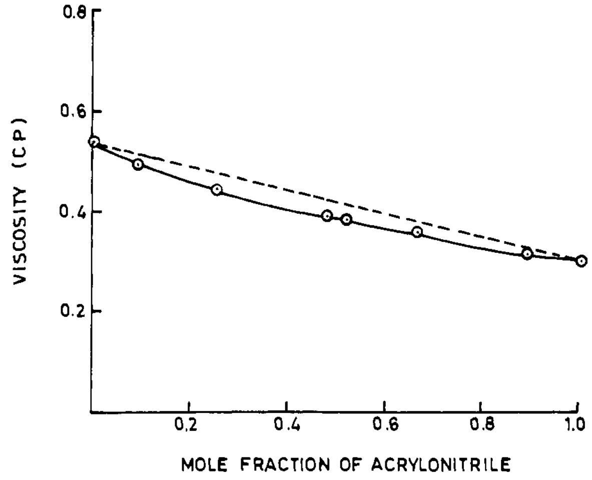

Figure 2. Variation of viscosity at 307.4 K with mole fraction of acrylonitrile in acrylonitrile-benzene mixture.

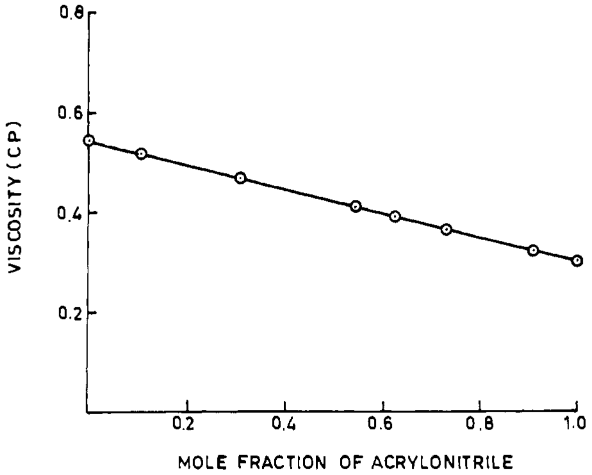

Figure 3. Variation of viscosity at 307.4 K with mole fraction of acrylonitrile in acrylonitrile-p-xylene mixture.

A perusal of the Figure 1 shows that there is an appreciable negative deviation from the rectilinear dependence or viscosity on mole fraction for the mixture containing cyclohexane as one of the components. The negative deviation is sufficiently reduced in the case of the acrylonitrile + benzene system. The deviations almost vanish when p-xylene and mersitylene are

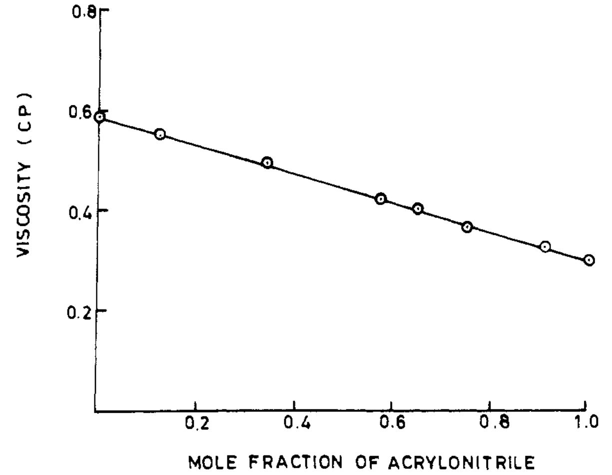

Figure 4. Variation of viscosity at 307.4 K with mole fraction of acrylonitrile in acrylonitrile–mesitylene mixture.

used as nonpolar components in the mixture.

It seems that in the case of acrylonitrile + cyclohexane binary liquid mixtures, the forces between unlike molecules are far less as compared to the forces between like molecules and that is why the mixture is more fluid, i.e., less viscous. This is quite likely in view of the known associating tendency of acrylonitrile. However, acrylonitrile + aromatic solvent mixtures of a certain composition become less fluid, i.e., more viscous, due to enhanced intermolecular forces between unlike molecules. This enhancement could be due to dipole-induced dipole interaction which is proportional to the polarizability of the aromatic molecule. The values of the polarizability of *p*-xylene and mesitylene are higher than that for benzene; the greater interaction of acrylonitrile with the former two aromatic solvents results in a higher viscosity as compared to benzene. Apparent linear dependence of mixture viscosity on molar proportion in the case of *p*-xylene and mesitylene could be fortuitous.

A perusal of Tables I–IV shows that the values of the parameter *d* are large and negative with cyclohexane, small and negative with benzene, and positive with *p*-xylene and mesitylene. Large negative values of *d* for the binary mixture with cyclohexane indicate the existence of weak interaction mainly due to dispersion forces. Increased (less negative) *d* values for the mixture with benzene indicate stronger interaction due to dipole-induced dipole interaction. Positive *d* values for the mixtures with *p*-xylene and mesitylene seem to be due to enhanced dipole-induced dipole interaction on account of higher polarizability of the methyl-substituted benzenes.

The values of W_{visc} have the following trend; highly positive with cyclohexane, less positive with benzene, negative with *p*-xylene, and more negative with mesitylene. This also supports the same contention as derived from *d* values.

Registry No. acrylonitrile, 107-13-1; cyclohexane, 110-82-7; benzene, 71-43-2; *p*-xylene, 106-42-3; mesitylene, 108-67-8.

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Solubility of Trialkyl Phosphate Adducts of Thorium Nitrate in Trialkyl Phosphate–Alkane Mixtures[†]

Robert J. Lemire* and Allan B. Campbell

Whiteshell Nuclear Research Establishment, Atomic Energy of Canada Limited, Pinawa, Manitoba, Canada R0E 1L0

Phase diagrams have been determined at 25 °C for several systems of the type $Th(NO_3)_4 \cdot x TAP$–TAP–alkane (where TAP ≡ trialkyl phosphate and $Th(NO_3)_4 \cdot x TAP$ is a solid adduct). The trimethyl phosphate (TMP) adduct has an extremely limited solubility in TMP solutions containing hexane. For the system $Th(NO_3)_4 \cdot 2.8TPP$–TPP–*n*-dodecane (TPP = tri-*n*-propyl phosphate), a substantial region of liquid–liquid immiscibility exists as well as an extensive invariant region. For the corresponding triisobutyl phosphate system, no region of liquid–liquid immiscibility was found. For the TPP system, the size of the region of immiscibility was found to be significantly smaller when *n*-octane or 2,2,4-trimethylpentane was used instead of *n*-dodecane. No solid thorium nitrate adducts of triethyl phosphate or tri-*n*-butyl phosphate (TBP) could be prepared, but phase separation was found in systems containing *n*-dodecane and anhydrous liquids with a TBP:$Th(NO_3)_4$ ratio close to 3.0:1.

Introduction

There is a large body of data in the chemical literature concerning the extraction of actinides from aqueous solutions using trialkyl phosphates (*1*–*3*). Most of these data are from experiments in which a nitrate salt was partitioned between organic and aqueous phases—often with a fixed composition mixture as the organic phase (e.g., 30% tri-*n*-butyl phosphate (TBP) in kerosene). The formation of a third liquid phase (i.e., phase separation of the predominantly organic liquid) has been reported in many cases, most notably in thorium nitrate–TBP–alkane diluent–water–nitric acid systems (*4*, *5*). The third liquid phase can cause substantial difficulties in extraction procedures during the reprocessing of thorium fuel for nuclear reactors.

There has been little systematic study of phase relationships in this five-component system, at least in part because no solid adducts of $Th(NO_3)_4$ with TBP have been reported. However, solid anhydrous adducts of $Th(NO_3)_4$ with other trialkyl phosphates have been synthesized (*6*, *7*). Thus, we decided to carry out a detailed study of phase relationships in simple anhydrous subsystems each containing only $Th(NO_3)_4$, a trialkyl phosphate (TAP) capable of forming a solid adduct with $Th(NO_3)_4$, and an alkane diluent. The work was then extended

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