

Volume and transport properties of binary liquid systems of acrylonitrile with aromatic ketones at 308.15 K

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The densities and viscosities for the binary mixtures of acrylonitrile with aromatic ketones (acetophenone, propiophenone, paramethyl acetophenone and parachloro acetophenone) have been reported over the entire range of mole fraction at 308.15 K. The excess molar volume (V^E) and deviation in viscosity ($\Delta\eta$) are fitted to a Redlich-Kister type equation. Other parameters like excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d') are also utilized in the qualitative analysis to elicit the information on the nature of the bulk molecular interactions of acrylonitrile + aromatic ketone binary mixtures.

Keywords: Density, Viscosity, Aromatic ketones, Acrylonitrile, Binary solvent mixtures

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Esters are used as plasticizing agents during polymer processing to impart favourable thermoplastic properties. Acrylonitrile is an important industrial solvent which is used as a monomer to synthesize polyacrylonitrile, a useful vinyl polymer that finds several applications. In addition to its use in polymer industry, it is also used as a chemical intermediate in the synthesis of antioxidants, pharmaceuticals, dyes, surface active agents. It is used as a pesticide fumigant for stored grain and experimentally to induce adrenal hemorrhagic necrosis in rats. Acetophenone and other aromatic ketones are used in the perfumery. It was, therefore, considered worthwhile to determine the parameters like excess molar volume (V^E), deviation in viscosity ($\Delta\eta$), excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan constant (d') of binary liquid mixtures of acrylonitrile with acetophenone (Aph), propiophenone (Pph), paramethyl acetophenone (Me-Aph) and parachloro acetophenone (Cl-Aph). The literature survey indicates that these parameters are not reported hitherto for the systems selected.

Experimental Procedure

All the four ketones (Aph, Pph, Me-Aph and Cl-Aph) purchased from SISCO Company, India, were dried over anhydrous potassium carbonate for three days. After three days they were filtered and distilled¹. The middle fractions of distillates were retained and

stored over 0.4 nm molecular sieves² to reduce the water content, if any, and to avoid the absorption of atmospheric moisture and carbon dioxide gas. High purity grade acrylonitrile (SISCO Company, India), was redistilled to eliminate the polymer formed on long standing before use³. The middle fraction of colourless liquid was collected and stored over 0.3 nm molecular sieves.

Deionised water (permutit process) was distilled twice. To each litre of distillate 0.2 g of potassium permanganate and 0.5 g of sodium hydroxide were added. This alkaline solution was slowly distilled from an all pyrex vessel followed by further distillation over sulphuric acid⁴. The electric conductance of distilled water was less than 1×10^{-6} ohm⁻¹ cm⁻¹.

Binary mixtures were prepared by mixing appropriate volumes of the liquid components in the specially designed glass bottles with air tight teflon coated caps and the mass measurements were performed on a Dhona 100 DS (India) single pan analytical balance with a precision of ± 0.01 mg. The required properties were measured on the same day immediately after preparing each composition. The uncertainty of the mole fraction was ± 0.0001 .

A double-arm pycnometer⁵ with a bulb of 10 mL and a capillary of an internal diameter of about 1 mm was used to measure the densities (ρ) of pure liquids and binary mixtures. The pycnometer was calibrated

by using conductivity water (conductivity less than $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$) with 0.9970 and 0.9940 g mL^{-1} as its densities at 298.15 and 308.15 K, respectively. The pycnometer filled with air bubble free liquids was kept in a thermostat (INSREF model IRI-071-India) with a thermal stability of $\pm 0.01 \text{ K}$ for 30 min to attain thermal equilibrium. The uncertainty of repeated density measurements affected the fourth decimal place. Experimental values of density for the pure liquids along with the literature values at 298.15 K are recorded in Table 1.

Ubbelohde viscometer⁶ having a capacity of about 15 mL and the capillary tube having a length of about 90 mm and 0.5 mm internal diameter was used to measure the flow times of pure liquids and liquid mixtures. The viscometer was then filled with the sample liquid by tilting the viscometer to about 30° from the vertical and its limbs were closed with teflon caps to avoid the evaporation. The viscometer was kept vertically in a transparent walled bath with a thermal stability of $\pm 0.01 \text{ K}$ for about 30 min to attain the thermal equilibrium. The efflux time between the marks on either side of the bulb was measured with a stopwatch of $\pm 0.1 \text{ s}$ precision. The uncertainty of viscosity was $\pm 0.005 \text{ mPa.s}$.

Results and Discussion

The densities and viscosities of the mixtures of acrylonitrile with Aph, Pph, Me-Aph and Cl-Aph and their corresponding excess molar volumes, deviations in viscosity, excess free energy of activation of viscous flow and Grunberg-Nissan interaction parameter along with the mole fraction of ketones are presented in Table 2.

The excess molar volumes (V^E) have been evaluated from density using the equations

$$V^E = V_m - (x_1 V_1 + x_2 V_2) \quad \dots(1)$$

$$V_m = (x_1 M_1 + x_2 M_2) / \rho_m \quad \dots(2)$$

Table 1 — Comparison of experimental densities (ρ) of pure liquids with literature values at 298.15 K

Component	$\rho/\text{g mL}^{-1}$	
	Expt.	Lit.
Acetophenone	1.0231	1.0225 ¹⁹
Propiophenone	1.0092	1.0087 ²⁰
Paramethyl acetophenone	0.9963*	—
Parachloro acetophenone	1.1889	1.1880 ²⁰
Acrylonitrile	0.8011	0.8004 ²¹

*Value at 308.15 K

where V_m and ρ_m are the molar volume and density of the mixture; x_1, V_1, M_1 and x_2, V_2 and M_2 are the mole fraction, molar volume and molecular weight of pure components 1 and 2, respectively.

From the values of density and efflux time the dynamic viscosity (η) of the sample liquid is calculated using the Eq.⁷

$$\frac{\eta}{\eta_w} = \frac{\rho t}{\rho_w t_w} \quad \dots(3)$$

where ρ, ρ_w and t, t_w are the density and flow time of the liquid and water, respectively, η_w represents the viscosity of water which is 0.72 mPa.s ⁶ at 308.15 K.

The deviation in viscosity is calculated by using the equation

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \quad \dots(4)$$

where η_m, η_1 and η_2 are viscosities of the liquid mixture and of the pure components 1 and 2, respectively; x_1 and x_2 are the mole fractions of the pure components 1 and 2 in the liquid state. The excess Gibbs free energy of activation of viscous flow (G^{*E}) is obtained by the equation

$$G^{*E} = RT [\ln \eta_m V_m - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \quad \dots(5)$$

where V_m is the molar volume of the mixture, R and T have their usual meanings.

Grunberg and Nissan⁸ formulated an important equation to assess the molecular interactions leading to viscosity changes. It is more reliable in reflecting the magnitude of molecular interactions at the site of interactions in molecules of a liquid state. Hence its assistance is resorted in the present study.

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d' \quad \dots(6)$$

where d' is a constant.

The excess properties y^E are fitted by the method of non-linear least squares to a Redlich-Kister type equation⁹

$$y^E = x_1 x_2 [a_0 + a_1 (x_1 - x_2) + a_2 (x_1 - x_2)^2] \quad \dots(7)$$

where a_0, a_1 and a_2 are the coefficients. The values of the coefficients and standard deviations (σ) are listed in Table 3. The standard deviations are calculated by using the equation

$$\sigma(y^E) = [\sum (y_{\text{obs}}^E - y_{\text{cal}}^E)^2 / (n - m)]^{1/2} \quad \dots(8)$$

Table 2 — Experimental densities (ρ), viscosities (η), excess molar volumes (V^E), deviation in viscosities ($\Delta\eta$), excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameters (d') at 308.15 K

x_1	$\rho/\text{g mL}^{-1}$	$\eta/\text{mPa.s}$	$V^E/\text{mL mol}^{-1}$	$\Delta\eta/\text{mPa.s}$	$G^{*E}/\text{kJ mol}^{-1}$	d'
Acetophenone (1) + Acrylonitrile (2)						
0.0000	0.7854	0.3296	—	—	—	—
0.0582	0.8128	0.3608	-0.6940	-0.0283	7.75	0.1519
0.1109	0.8338	0.3946	-0.8168	0.0483	20.54	0.2384
0.1957	0.8636	0.4532	-0.8672	-0.0762	36.64	0.2701
0.2736	0.8873	0.5132	-0.8803	-0.0960	48.64	0.2853
0.3939	0.9186	0.6200	-0.8405	-0.1120	63.37	0.3187
0.4591	0.9334	0.6760	-0.7894	-0.1225	61.22	0.2847
0.5681	0.9553	0.7844	-0.6999	-0.1256	58.30	0.2668
0.6945	0.9774	0.9222	-0.5498	-0.1164	45.62	0.2312
0.7954	0.9929	1.0519	-0.3248	-0.0903	35.31	0.2352
1.0000	1.0200	1.3512	—	—	—	—
Propiophenone (1) + Acrylonitrile (2)						
0.0000	0.7854	0.3296	—	—	—	—
0.1051	0.8327	0.4050	-0.5991	-0.0442	41.38	0.5228
0.1752	0.8581	0.4545	-0.8062	-0.0752	53.99	0.4055
0.2496	0.8811	0.5130	-0.9692	-0.1008	65.58	0.3713
0.3126	0.8981	0.5731	-1.0496	-0.1124	78.62	0.4012
0.4246	0.9237	0.6893	-1.0810	-0.1238	91.37	0.4236
0.5385	0.9446	0.8078	-0.9734	-0.1350	84.55	0.3699
0.6672	0.9638	0.9571	-0.7462	-0.1322	67.53	0.3120
0.8184	0.9824	1.1612	-0.4199	-0.1002	38.80	0.2471
1.0000	1.0006	1.4682	—	—	—	—
Paramethyl acetophenone (1) + Acrylonitrile (2)						
0.0000	0.7854	0.3296	—	—	—	—
0.0530	0.8147	0.3650	-0.6940	-0.0286	15.30	0.4048
0.1107	0.8364	0.4026	-0.8168	-0.0606	28.60	0.3016
0.1749	0.8574	0.4516	-0.8672	-0.0891	45.60	0.3165
0.2487	0.8784	0.5110	-0.8803	-0.1188	57.87	0.2978
0.3327	0.8989	0.5909	-0.8405	-0.1403	72.37	0.3220
0.4237	0.9183	0.6840	-0.7894	-0.1569	78.80	0.3192
0.5360	0.9388	0.8136	-0.6999	-0.1629	78.89	0.3156
0.6679	0.9589	0.9939	-0.5498	-0.1417	72.85	0.3413
0.8181	0.9777	1.2303	-0.3248	-0.0866	52.46	0.3887
1.0000	0.9963	1.5364	—	—	—	—
Parachloro acetophenone (1) + Acrylonitrile (2)						
0.0000	0.7854	0.3296	—	—	—	—
0.0547	0.8340	0.3753	-0.6940	-0.0618	16.56	0.4575
0.1146	0.8758	0.4278	-0.8168	-0.1267	31.87	0.3805
0.1793	0.9155	0.4934	-0.8672	-0.1883	48.22	0.3780
0.2555	0.9565	0.5751	-0.8803	-0.2562	57.36	0.3208
0.3377	0.9953	0.6821	-0.8405	-0.3105	67.94	0.3232
0.4269	1.0321	0.8190	-0.7894	-0.3487	76.06	0.3359
0.5441	1.0737	1.0260	-0.6999	-0.3718	74.25	0.3234
0.6719	1.1107	1.3028	-0.5498	-0.3459	65.56	0.3228
0.8213	1.1473	1.6974	-0.3248	-0.2447	41.48	0.3123
1.0000	1.1813	2.2929	—	—	—	—

Table 3 — Coefficients (a) and standard deviations (σ) of aromatic ketones + acrylonitrile systems at 308.15 K

Binary system	Property	Coefficients			Deviations
		a_0	a_1	a_2	σ
Acetophenone (1)+Acrylonitrile (2)	$V^E/\text{mL mol}^{-1}$	-3.3718	3.0810	-0.2789	0.1878
	$\Delta\eta/\text{mPa.s}$	0.5669	-0.0877	-0.1510	0.0539
Propiophenone (1)+Acrylonitrile (2)	$V^E/\text{mL mol}^{-1}$	-4.2096	2.2970	-0.2071	0.0844
	$\Delta\eta/\text{mPa.s}$	-0.7290	-0.2137	-0.5852	0.1794
Paramethyl acetophenone (1) +Acrylonitrile (2)	$V^E/\text{mL mol}^{-1}$	-3.8988	5.7801	-0.4198	0.4603
	$\Delta\eta/\text{mPa.s}$	-0.5301	0.0702	0.2444	0.0893
Parachloro acetophenone (1)+Acrylonitrile (2)	$V^E/\text{mL mol}^{-1}$	-5.5987	4.9222	-0.4439	0.4462
	$\Delta\eta/\text{mPa.s}$	-1.4486	-0.2782	0.0776	0.0257

where n is the total number of experimental points and m is the number of coefficients. The plots of excess molar volume and deviation in viscosity versus mole fraction of ketones (x_1) are shown in Figs 1 and 2, respectively.

Volume

All the isotherms at 308.15 K for the systems of acrylonitrile with four ketones are parabolic in nature indicating negative deviations over the entire range of mole fraction.

The observed V^E values are the resultant of physical and chemical forces and they may be broadly recognized as: (i) The breaking of liquid order on mixing with the second component; (ii) Non-specific physical interactions and unfavourable interactions between unlike molecules; (iii) Specific interactions appearing in the mixture between dissimilar molecules by dipole-dipole and; (iv) Specific interactions appearing in the mixture between solvent and cosolvent molecules by electron donor-acceptor complexes.

For the systems studied, the effects identified through the analysis of excess molar volume and deviation in viscosity are presented below.

The first two factors contribute for the expansion of volume and the latter two factors contribute to the contraction of the volume. From the isothermal curves at 308.15 K shown in Fig. 1, it is clear that in the case of acrylonitrile with phenones, the volume reduction factors have got an ascendancy over the expansion factors.

All the phenones studied are strongly dipolar solvents. Due to strong dipoles all the phenones, acetophenone, propiophenone, paramethyl acetophenone and parachloro acetophenone are associated liquids¹⁰. Hence, when acrylonitrile is mixed with the phenones, dissociation of associated

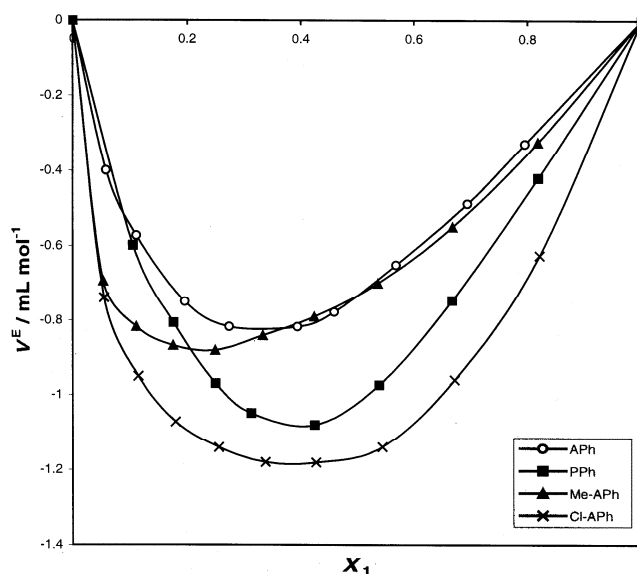


Fig. 1 — Variation of V^E of the binary liquid mixtures of acrylonitrile (2) with acetophenone (1); propiophenone (1); paramethyl acetophenone (1) and parachloro acetophenone (1) at 308.15 K

liquid structure takes place resulting in an expansion of volume of mixtures. The shape and size of the phenones and their cosolvent are not identical or similar. So, on mixing the solvents non-specific physical interactions and unfavourable interactions between the molecules of unlike components come into play increasing the volume of binary solvent mixtures.

Acrylonitrile is also a strongly associated liquid with the parallel and antiparallel orientation of its molecules¹¹. So, when it is mixed with the second component (phenones) it also loses its conglomerates contributing to the expansion of volume. Therefore, there will be a mutual loss of dipolar association of phenone solvents and acrylonitrile solvent on mixing.

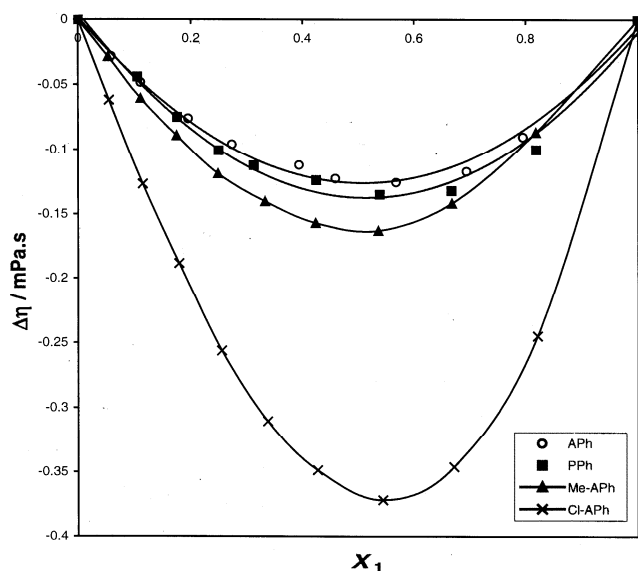


Fig. 2 — Variation of $\Delta\eta$ of the binary liquid mixtures of acrylonitrile (2) with acetophenone (1); propiophenone (1); paramethyl acetophenone (1) and parachloro acetophenone (1) at 308.15 K

All phenones are dipolar aprotic solvents. Similarly, acrylonitrile is also dipolar aprotic solvent. Acrylonitrile, due to its high dipole moment¹² (1.17×10^{-29} C m) favours dipole-dipole interactions. Hence, there will be dipole-dipole interactions between unlike molecules of the four systems, contributing to the reduction in the volume. From the above argument and Fig. 1 it is clear that the specific interactions are present between the mixtures of phenones and acrylonitrile.

In addition to the above strong dipole-dipole interactions, there may be a possibility of electron donor-acceptor complex formation between phenones and π -electron cloud of acrylonitrile. Here the oxygen atom of ketoxy group of phenones accepts the electrons into its $2p$ level vacant molecular orbital¹³ and acrylonitrile easily donates its mobile π -electrons. In parachloro acetophenone the charge transfer complex formation is still predominant due to highly electronegative chlorine atom present in it. Hence, the deeper minima is observed in the isotherm of parachloro acetophenone.

In parachloro acetophenone, there is a mesomeric effect, i.e., conjugation between π -electrons of phenyl ring and unshared electron pair of chlorine atom. Though chlorine is having $-I$ effect (inductive effect), withdrawing electrons from phenyl ring of parachloro acetophenone, the mesomeric effect releasing electrons into benzene ring dominates over the $-I$

inductive effect. Because of this reason, the electron density on the ketoxy oxygen of parachloro acetophenone is greater than that of acetophenone.

In paramethyl acetophenone, there is a mesomeric effect due to hyperconjugation between hydrogen atom of methyl substituent and π -electrons of phenyl ring. This is also called as nobond resonance. Because of this reason the electron density on the carbonyl oxygen is greater than acetophenone.

When the electron density of oxygen atom of ketoxy group is compared between parachloro acetophenone and paramethyl acetophenone, the parachloro acetophenone stands first. This is because the unpaired electron pair on chlorine atom is more free than the bonded electron pair of hydrogen atom. Hence, the parachloro acetophenone must have higher electron density than paramethyl acetophenone at the site of molecular interaction. Therefore, the order of interaction for these three phenones is

$$\text{Cl-Aph} > \text{Me-Aph} > \text{Aph}$$

In case of propiophenone, due to the presence of ethyl group, its $+I$ effect is more than acetophenone having methyl group. The greater $+I$ effect is experimentally confirmed on interaction energetic ground¹⁴. Based on this argument, the interaction position of propiophenone may fall between acetophenone and paramethyl acetophenone. Therefore, the total molecular interaction order of four phenones should be

$$\text{Cl-Aph} > \text{Me-Aph} > \text{Pph} > \text{Aph}$$

Experimentally observed V^E values are not in similar lines of polarity conjecture mentioned above. Experimentally observed order at the composition of optimum molecular interaction is:

$$\text{Cl-Aph} > \text{Pph} > \text{Me-Aph} > \text{Aph}$$

But at the equimolar composition $x_1 = 0.5$, the order becomes

$$\text{Cl-Aph} > \text{Pph} > \text{Me-Aph} = \text{Aph}$$

Viscosity

The viscosity measurements were carried out in order to illuminate on the order of molecular interactions. A correlation between the sign of $\Delta\eta$ and V^E has been observed for a binary solvent system, $\Delta\eta$

being positive where V^E is negative or vice-versa¹⁵. Figs 1 and 2 clearly indicate that the isotherms of V^E and $\Delta\eta$ do not obey the above general statement. Therefore, the strength of the specific or dispersion forces is not the only factor influencing the viscosity deviation of liquid mixtures. The molecular size and shapes of the components are also equally important. Rastogi *et al.*¹⁶, therefore, suggested that the observed excess property is a combination of an interaction and a non-interaction part. Thus, one may write,

$$X^E_{(\text{observed})} = X^E_{(\text{interaction})} + X^E_{(\text{size effect})}$$

where $X^E_{(\text{observed})}$ refers to the excess or deviation in the property. The non-interaction part in the form of size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. Based on this theory, the observed negative $\Delta\eta$ values may be due to smaller size of acrylonitrile molecule as compared to phenones.

In order to elucidate the forces that are acting between unlike molecules, the help of excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d') has become indispensable and quintessential. According to Reed and Taylor¹⁷ and Meyer *et al.*¹⁸, positive G^{*E} values indicate specific interactions while negative values indicate the dominance of dispersion forces; similarly, if d' values are positive the interactions between unlike molecules are strong whereas weak with negative values. The values of Table 2 incontrovertibly indicate that G^{*E} and d' are positive for all the systems over the entire range of mole fraction. Hence, a cerebral conclusion can be made that chemical forces are dominating over the physical forces in all the systems.

The negative $\Delta\eta$ values at equimolar concentration of acrylonitrile and phenones follow the order:



This order confirms the theoretical contemplation of the magnitude of polarity on the carbonyl functionality of four aromatic ketones selected for investigations, because the deviation parameters are considered to be the reflecting agents of the polarity sinew at the site of interactions in the molecules.

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