Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Acrylonitrile with Methyl Acetate, Ethyl Acetate, *n*-Propyl Acetate, *n*-Butyl Acetate, and 3-Methylbutyl-2-acetate in the Temperature Interval (298.15−308.15) K

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Experimental values of density, viscosity, and refractive index at (298.15, 303.15, and 308.15) K and the speed of sound at 298.15 K for the binary mixtures of acrylonitrile with methyl acetate, ethyl acetate, propyl acetate, butyl acetate, and 3-methylbutyl-2-acetate are presented over the whole range of mixture composition. From these data, excess molar volume, deviations in viscosity, speed of sound, isentropic compressibility, and Lorenz−Lorentz molar refractivity have been calculated. These results are fitted to Redlich−Kister type polynomial equation of the third degree to derive the binary coefficients. The standard error values are estimated between the calculated and experimental data.

Introduction

Acrylonitrile is an important industrial solvent that is used as a monomer to synthesize polyacrylonitrile, a useful vinyl polymer that finds several applications. Esters are used as plasticizing agents during polymer processing to impart favorable thermoelastic properties. A fundamental understanding of the mixing behavior of acrylonitrile with esters is therefore important from a technical and engineering viewpoint. In the recent literature, only a few studies (Sandhu and Singh, 1992; Haijun et al., 1994) have been made on the thermodynamic properties of binary mixtures containing acrylonitrile. To the best of our knowledge, no extensive studies have been made on the mixtures of acrylonitrile with esters. Herein, we report the results of density, ρ, viscosity, η, refractive index, n_D with the sodium D-line, and speed of sound, u, for the binary mixtures of acrylonitrile with methyl acetate, ethyl acetate, propyl acetate, butyl acetate, and 3-methylbutyl-2-acetate over the entire range of mixture composition. The values of u are measured only at 298.15 K, while those of ρ, η, and n_D are measured at (298.15, 303.15, and 308.15) K. Using these data, excess molar volume, V^E, deviations in viscosity, $\Delta\eta$, speed of sound, Δu, isentropic compressibility, Δk_S, and Lorenz−Lorentz molar refractivity, ΔR, have been computed. The results are graphically presented and compared with values calculated from the Redlich−Kister type polynomial equation. The standard deviations for the least-squares fittings are also presented for all the mixtures and at all the temperatures.

Experimental Section

Materials. High-purity spectroscopic and analytical grade samples of acrylonitrile, methyl acetate, ethyl acetate, and 3-methylbutyl-2-acetate were procured from S.D. Fine Chemicals Ltd., Mumbai, India. Propyl acetate and butyl acetate were purchased from E. Merck. All the samples were used without further purification because their purities exceeded 99% as tested by gas chromatography (HP 6890 series) using a flame ionization detector with a packed column (see Table 1). Experimental values of ρ and n_D of the pure liquids are compared in Table 1 at 298.15 K, and these values agree well with the published results. Mixtures were prepared by mass in specially designed glass stoppered bottles and were used on the same day. An electronic Mettler balance, model AE 240, with a precision of ±0.01 mg was used. The error in mole fraction was around ±0.0002.

Measurements. Densities of liquids and their mixtures were measured using the pycnometer having a bulb volume of 15 cm^3 and a capillary bore with an internal diameter of 1 mm. Density values are accurate to ±0.0002 $g{\cdot}cm^{-3}$.

Refractive indices for the sodium D-line were measured using a thermostatically controlled Abbe Refractometer (Atago 3T, made in Japan). A minimum of three independent readings were taken for each composition. The refractive index values are accurate to ±0.0001 units. Calibration procedures of the pycnometer and refractometer are the same as given earlier (Aminabhavi et al., 1993; Aminabhavi and Bindu, 1994; Aralaguppi et al., 1991).

Viscosities were measured using a Cannon Fenske Viscometer (size 75, Industrial Research Glassware, Ltd., Rosella, NJ). An electronic digital stopwatch with a readability of ±0.01 s was used for the flow time measurements. The measured viscosity values are accurate to ±0.001 mPa·s. Calibration of the viscometer is the same as described earlier (Aminabhavi and Bindu, 1994; Aminabhavi et al., 1993; Aralaguppi et al., 1991).

The speed of sound values were measured using a variable path single-crystal interferometer (Mittal Enterprises, model M-84, New Delhi) as described earlier by Aralaguppi et al. (1991). The interferometer was used at a frequency of 4 kHz and was calibrated using water and benzene. The speed of sound values are accurate to ±2 $m{\cdot}s^{-1}$. From the speed of sound data, the values of isentropic compressibilities, k_S, have been calculated from $k_S = 1/u^2\rho$.

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Table 1. Comparison of Experimental Densities (ρ) and Refractive Indices (n_D) of the Pure Liquids with Literature Values at 298.15 K

liquid (mol % purity)	ρ/g·cm^{-3} exptl	ρ/g·cm^{-3} lit.	n_D exptl	n_D lit.	references
acrylonitrile (99.4)	0.8002	0.8003[a]	1.3920	1.3888[b]	Haijun et al. (1994); Riddick et al. (1986)
methyl acetate (99.2)	0.9282	0.9268	1.3606	1.3589	Yoshikawa et al. (1991)
ethyl acetate (99.4)	0.8948	0.8943	1.3710	1.3701	Ortega et al. (1987)
propyl acetate (99.3)	0.8824	0.8827	1.3832	1.3838	Correa et al. (1991)
butyl acetate (99.5)	0.8753	0.8762	1.3934	1.3936	Correa et al. (1991)
3-methylbutyl-2-acetate (99.1)	0.8660	N/A	1.3991	N/A	

[a] Haijun et al. (1994). [b] Riddick et al. (1986). [c] N/A: not available for comparison.

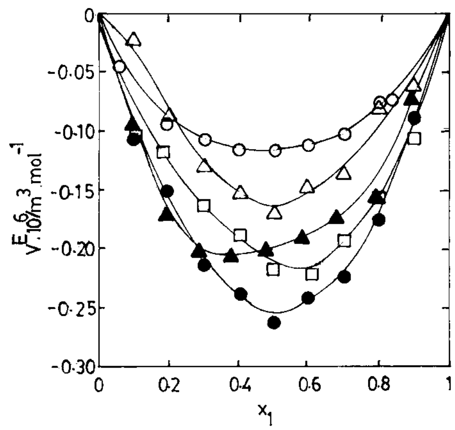

Figure 1. Plots of excess molar volume vs mole fraction of acrylonitrile at 298.15 K for the mixtures of acrylonitrile with (○) methyl acetate, (△) ethyl acetate, (□) propyl acetate, (●) butyl acetate, and (▲) 3-methylbutyl-2-acetate.

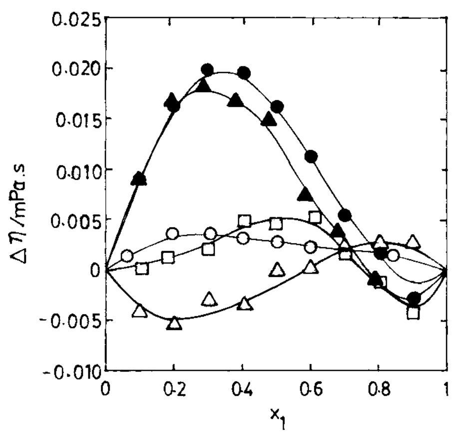

Figure 2. Plots of deviation in viscosity vs mole fraction of acrylonitrile at 298.15 K for the same mixtures given in Figure 1.

In all the property measurements, an INSREF, model 016 AP thermostat was used and the desired temperature was controlled within ±0.01 K. The results of ρ, η, n_D, and u compiled in Table 2 represent the averages of three independent measurements for each composition of the mixture.

The Julabo immersion cooler (FT 200), Julabo Labortechnik Gmbh, Germany was employed to cool the water bath. This unit was installed at the intake of a heating circulator to draw the heat away from the circulating bath liquid. The immersion probe was connected to the instrument with a flexible and insulated tube. To prevent the immersion probe from icing, it was completely immersed into the bath liquid.

Results and Discussion

From the results of densities given in Table 2, excess molar volumes have been calculated as

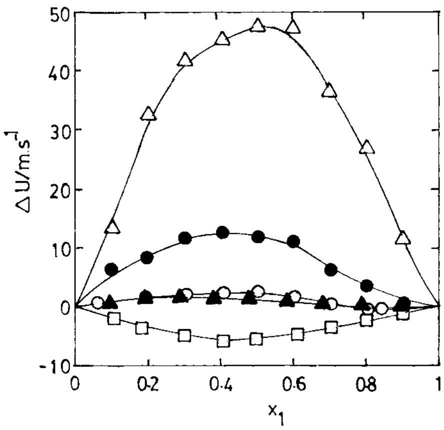

Figure 3. Plots of deviation in speed of sound vs mole fraction of acrylonitrile at 298.15 K for the same mixtures given in Figure 1.

$$V^E/m^3 \cdot mol^{-1} = V_m - V_1x_1 - V_2x_2 \quad (1)$$

where V_m is the mixture molar volume, V_1 and V_2 are the molar volumes of components 1 and 2 of the mixture, and x_i represents the mole fraction of the ith component in the mixture. From the values of η, n_D, u, and k_S of the individual components as well as of the binary mixtures, $\Delta\eta$, ΔR, Δu, and Δk_S have been calculated from

$$\Delta Y = Y_m - Y_1c_1 - Y_2c_2 \quad (2)$$

For calculating $\Delta\eta$ and Δu, we have used the mole fractions, x_i, for c_i. Similarly, following the conventional practice in the literature (Aralaguppi et al., 1991), to compute ΔR and Δk_S, the volume fraction, ϕ_i [$=(x_1V_1)/(\sum x_iV_i)$] was used.

Each set of excess functions have been fitted to Redlich–Kister (1948) type polynomial equation

$$V^E \text{ (or } \Delta Y) = c_1c_2\sum_{j=1}^{k}A_j(c_2 - c_1)^{j-1} \quad (3)$$

to estimate the parameter values A_0, A_1, and A_2 by the method of least squares using the Marquardt algorithm (1963). It was found that the best fittings were obtained for the solution of eq 3 with only three adjustable parameters.

The standard deviations, σ, between the fitted quantities (eq 3) and the computed quantities (eqs 1 and 2) were calculated using

$$\sigma = \left(\frac{\sum(V^E_{cal} \text{ (or } \Delta Y_{cal}) - V^E_{obs} \text{ (or } \Delta Y_{obs}))}{(n - m)}\right)^{1/2} \quad (4)$$

where n represents the number of data points and m the number of coefficients. The fitted parameter values along

Table 2. Experimental Values of Density (ρ), Refractive Index (n_D), Viscosity (η), and Speed of Sound (u) of the Binary Mixtures at Different Temperatures

x_1	ρ/(g·cm^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})	x_1	ρ/(g·cm^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})	x_1	ρ/(g·cm^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})
							Acrylonitrile (1) + Methyl Acetate (2)							
							298.15 K							
0.0000	0.9282	1.3606	0.391	1161	0.4041	0.8834	1.3720	0.375	1179	0.8037	0.8302	1.3838	0.355	1192
0.0617	0.9221	1.3622	0.389	1164	0.5024	0.8712	1.3749	0.370	1183	0.8416	0.8247	1.3851	0.353	1194
0.1961	0.9077	1.3655	0.385	1170	0.6004	0.8585	1.3778	0.365	1186	1.0000	0.8002	1.3920	0.344	1200
0.3042	0.8954	1.3689	0.380	1175	0.7033	0.8445	1.3808	0.360	1189					
							303.15 K							
0.0000	0.9218	1.3592	0.372		0.4041	0.8774	1.3692	0.357		0.8037	0.8246	1.3806	0.336	
0.0617	0.9158	1.3597	0.371		0.5024	0.8654	1.3720	0.353		0.8416	0.8191	1.3822	0.333	
0.1961	0.9013	1.3638	0.367		0.6004	0.8526	1.3750	0.348		1.0000	0.7949	1.3866	0.324	
0.3042	0.8892	1.3672	0.362		0.7033	0.8389	1.3781	0.343						
							308.15 K							
0.0000	0.9152	1.3550	0.355		0.4041	0.8712	1.3664	0.345		0.8037	0.8179	1.3780	0.322	
0.0617	0.9080	1.3569	0.354		0.5024	0.8594	1.3692	0.340		0.8416	0.8135	1.3794	0.319	
0.1961	0.8939	1.3608	0.351		0.6004	0.8450	1.3712	0.335		1.0000	0.7893	1.3844	0.309	
0.3042	0.8826	1.3638	0.349		0.7033	0.8330	1.3752	0.330						
							Acrylonitrile (1) + Ethyl Acetate (2)							
							298.15 K							
0.0000	0.8948	1.3710	0.457	1144	0.4047	0.8666	1.3777	0.408	1212	0.8021	0.8265	1.3857	0.369	1216
0.1002	0.8884	1.3728	0.442	1163	0.5034	0.8582	1.3800	0.400	1220	0.9003	0.8143	1.3882	0.358	1206
0.2025	0.8818	1.3744	0.429	1188	0.5994	0.8489	1.3816	0.390	1225	1.0000	0.8002	1.3920	0.344	1200
0.3034	0.8746	1.3763	0.420	1203	0.7007	0.8384	1.3836	0.381	1220					
							303.15 K							
0.0000	0.8886	1.3681	0.437		0.4047	0.8606	1.3756	0.387		0.8021	0.8210	1.3830	0.358	
0.1002	0.8822	1.3699	0.419		0.5034	0.8521	1.3767	0.379		0.9003	0.8081	1.3852	0.349	
0.2025	0.8757	1.3715	0.403		0.5994	0.8431	1.3786	0.368		1.0000	0.7949	1.3866	0.324	
0.3034	0.8685	1.3730	0.397		0.7007	0.8327	1.3806	0.364						
							308.15 K							
0.0000	0.8825	1.3657	0.421		0.4047	0.8539	1.3720	0.369		0.8021	0.8140	1.3801	0.344	
0.1002	0.8757	1.3674	0.398		0.5034	0.8454	1.3742	0.361		0.9003	0.8019	1.3822	0.328	
0.2025	0.8689	1.3688	0.383		0.5994	0.8365	1.3762	0.352		1.0000	0.7893	1.3844	0.309	
0.3034	0.8617	1.3708	0.377		0.7007	0.8258	1.3778	0.351						
							Acrylonitrile (1) + Propyl Acetate (2)							
							298.15 K							
0.0000	0.8824	1.3832	0.563	1181	0.4057	0.8610	1.3861	0.479	1183	0.8019	0.8267	1.3888	0.387	1194
0.1052	0.8781	1.3842	0.540	1181	0.4982	0.8547	1.3866	0.459	1185	0.9010	0.8146	1.3895	0.362	1197
0.1835	0.8740	1.3848	0.524	1181	0.6097	0.8458	1.3874	0.435	1188	1.0000	0.8002	1.3920	0.344	1200
0.2994	0.8677	1.3854	0.500	1182	0.7023	0.8372	1.3882	0.411	1191					
							303.15 K							
0.0000	0.8767	1.3807	0.524		0.4057	0.8553	1.3834	0.452		0.8019	0.8210	1.3862	0.368	
0.1052	0.8723	1.3817	0.504		0.4982	0.8489	1.3840	0.434		0.9010	0.8088	1.3870	0.345	
0.1835	0.8683	1.3823	0.489		0.6097	0.8399	1.3846	0.411		1.0000	0.7949	1.3866	0.324	
0.2994	0.8618	1.3826	0.470		0.7023	0.8315	1.3853	0.391						
							308.15 K							
0.0000	0.8713	1.3783	0.489		0.4057	0.8496	1.3808	0.428		0.8019	0.8147	1.3832	0.352	
0.1052	0.8669	1.3787	0.472		0.4982	0.8430	1.3814	0.411		0.9010	0.8029	1.3838	0.331	
0.1835	0.8629	1.3793	0.460		0.6097	0.8340	1.3823	0.392		1.0000	0.7893	1.3844	0.309	
0.2994	0.8563	1.3798	0.442		0.7023	0.8254	1.3828	0.372						
							Acrylonitrile (1) + Butyl Acetate (2)							
							298.15 K							
0.0000	0.8753	1.3934	0.675	1192	0.4040	0.8582	1.3932	0.561	1208	0.8014	0.8269	1.3926	0.412	1202
0.0990	0.8721	1.3933	0.651	1199	0.5006	0.8525	1.3932	0.526	1208	0.9031	0.8144	1.3924	0.374	1200
0.1971	0.8682	1.3932	0.626	1202	0.5992	0.8454	1.3931	0.488	1208	1.0000	0.8002	1.3920	0.344	1200
0.2999	0.8637	1.3932	0.596	1206	0.7004	0.8370	1.3929	0.449	1204					
							303.15 K							
0.0000	0.8704	1.3908	0.631		0.4040	0.8530	1.3907	0.524		0.8014	0.8213	1.3892	0.384	
0.0990	0.8670	1.3908	0.607		0.5006	0.8470	1.3905	0.490		0.9031	0.8089	1.3883	0.349	
0.1971	0.8629	1.3907	0.582		0.5992	0.8399	1.3905	0.458		1.0000	0.7949	1.3866	0.324	
0.2999	0.8584	1.3907	0.553		0.7004	0.8314	1.3897	0.421						
							308.15 K							
0.0000	0.8654	1.3882	0.593		0.4040	0.8477	1.3880	0.494		0.8014	0.8149	1.3864	0.365	
0.0990	0.8618	1.3882	0.571		0.5006	0.8417	1.3880	0.464		0.9031	0.8027	1.3856	0.330	
0.1971	0.8576	1.3882	0.547		0.5992	0.8345	1.3878	0.433		1.0000	0.7893	1.3844	0.309	
0.2999	0.8532	1.3882	0.522		0.7004	0.8260	1.3870	0.398						
							Acrylonitrile (1) + 3-Methylbutyl-2-acetate (2)							
							298.15 K							
0.0000	0.8660	1.3991	0.795	1198	0.3796	0.8535	1.3976	0.641	1200	0.7861	0.8268	1.3942	0.440	1200
0.0960	0.8636	1.3990	0.761	1199	0.4771	0.8486	1.3970	0.595	1200	0.8940	0.8149	1.3924	0.388	1200
0.1903	0.8609	1.3986	0.726	1200	0.5820	0.8425	1.3964	0.540	1200	1.0000	0.8002	1.3920	0.344	1200
0.2870	0.8574	1.3982	0.684	1200	0.6783	0.8358	1.3954	0.493	1200					
							303.15 K							
0.0000	0.8612	1.3968	0.740		0.3796	0.8484	1.3952	0.601		0.7861	0.8213	1.3915	0.417	
0.0960	0.8586	1.3967	0.710		0.4771	0.8435	1.3946	0.558		0.8940	0.8097	1.3884	0.370	
0.1903	0.8558	1.3962	0.681		0.5820	0.8372	1.3935	0.510		1.0000	0.7949	1.3866	0.324	
0.2870	0.8523	1.3958	0.641		0.6783	0.8306	1.3928	0.465						
							308.15 K							
0.0000	0.8564	1.3942	0.690		0.3796	0.8434	1.3929	0.565		0.7861	0.8159	1.3884	0.396	
0.0960	0.8538	1.3940	0.663		0.4771	0.8384	1.3920	0.526		0.8940	0.8043	1.3867	0.353	
0.1903	0.8509	1.3937	0.639		0.5820	0.8321	1.3911	0.480		1.0000	0.7893	1.3844	0.309	
0.2870	0.8473	1.3932	0.604		0.6783	0.8253	1.3900	0.440						

Table 3. Estimated Parameters of Excess Functions for Mixtures

function	temp/K	A_0	A_1	A_2	σ
Acrylonitrile (1) + Methyl Acetate (2)					
$V^E/10^{-6}$ (m^3·mol^{-1})	298.15	−0.463	−0.063	−0.254	0.004
	303.15	−0.470	−0.036	−0.100	0.008
	308.15	−0.393	0.134	0.738	0.068
$\Delta\eta$/(mPa·s)	298.15	0.011	0.010	0.013	0.000
	303.15	0.026	−0.011	0.001	0.004
	308.15	0.035	0.007	−0.021	0.001
$\Delta R/10^{-6}$ (m^3·mol^{-1})	298.15	−0.445	−0.112	−0.457	0.004
	303.15	−0.372	0.139	−0.161	0.020
	308.15	−0.347	−0.102	0.377	0.008
Δu/(m·s^{-1})	298.15	8.81	8.79	−13.53	0.175
Δk_S/(TPa^{-1})	298.15	−39.3	16.0	12.9	0.256
Acrylonitrile (1) + Ethyl Acetate (2)					
$V^E/10^{-6}$ (m^3·mol^{-1})	298.15	−0.659	0.062	0.325	0.012
	303.15	−0.634	0.036	0.519	0.017
	308.15	−0.325	−0.103	1.124	0.008
$\Delta\eta$/(mPa·s)	298.15	−0.003	−0.041	−0.010	0.001
	303.15	−0.008	−0.095	0.041	0.003
	308.15	−0.016	−0.126	0.006	0.003
$\Delta R/10^{-6}$ (m^3·mol^{-1})	298.15	−2.681	0.293	−0.178	0.010
	303.15	−2.504	0.589	0.232	0.015
	308.15	−2.485	0.547	0.174	0.011
Δu/(m·s^{-1})	298.15	195.4	19.2	−56.2	2.07
Δk_S/(TPa^{-1})	298.15	−296.1	146.1	10.9	2.81
Acrylonitrile (1) + Propyl Acetate (2)					
$V^E/10^{-6}$ (m^3·mol^{-1})	298.15	−0.832	0.160	−0.288	0.012
	303.15	−0.763	0.063	−0.148	0.014
	308.15	−0.622	−0.210	0.007	0.015
$\Delta\eta$/(mPa·s)	298.15	0.021	0.012	−0.062	0.001
	303.15	0.040	−0.008	−0.048	0.001
	308.15	0.048	−0.014	−0.037	0.001
$\Delta R/10^{-6}$ (m^3·mol^{-1})	298.15	−6.286	1.425	−0.570	0.008
	303.15	−6.117	1.803	−0.131	0.006
	308.15	−6.051	1.777	−0.715	0.009
Δu/(m·s^{-1})	298.15	−21.6	−7.5	8.6	0.189
Δk_S/(TPa^{-1})	298.15	−4.5	−23.3	6.4	0.305
Acrylonitrile (1) + Butyl Acetate (2)					
$V^E/10^{-6}$ (m^3·mol^{-1})	298.15	−1.017	0.048	−0.081	0.009
	303.15	−0.851	0.037	0.143	0.012
	308.15	−0.841	−0.170	1.021	0.023
$\Delta\eta$/(mPa·s)	298.15	0.066	0.082	−0.037	0.001
	303.15	0.059	0.065	−0.070	0.001
	308.15	0.055	0.065	−0.081	0.001
$\Delta R/10^{-6}$ (m^3·mol^{-1})	298.15	−10.8	3.8	−1.51	0.012
	303.15	−10.6	3.8	−1.37	0.013
	308.15	−10.6	3.8	−1.23	0.011
Δu/(m·s^{-1})	298.15	48.7	28.9	−23.7	0.763
Δk_S/(TPa^{-1})	298.15	−67.1	82.5	−31.2	0.971
Acrylonitrile (1) + 3-Methylbutyl-2-acetate (2)					
$V^E/10^{-6}$ (m^3·mol^{-1})	298.15	−0.817	−0.180	−0.379	0.010
	303.15	−0.716	−0.133	−0.152	0.009
	308.15	−0.681	−0.115	−0.095	0.008
$\Delta\eta$/(mPa·s)	298.15	0.052	0.096	−0.023	0.001
	303.15	0.061	0.078	0.024	0.001
	308.15	0.064	0.081	0.034	0.002
$\Delta R/10^{-6}$ (m^3·mol^{-1})	298.15	−16.1	6.4	−3.2	0.016
	303.15	−16.0	6.4	−3.2	0.010
	308.15	−16.0	6.4	−2.9	0.019
Δu/(m·s^{-1})	298.15	5.1	6.2	2.2	0.131
Δk_S/(TPa^{-1})	298.15	−16.0	12.6	−21.0	0.350

with the standard deviations are presented in Table 3. It is to be noted that in Figures 1 to 5, the best solid lines (eq 3) are drawn from the smoothed computed values, whereas the points represent those calculated from eqs 1 and 2.

Excess molar volumes of acrylonitrile + esters displayed in Figure 1 at 298.15 K are negative for all the mixtures, and these show a decreasing tendency with increasing size of the ester molecules. The negative values of V^E vary in the following order: methyl acetate < ethyl acetate < propyl acetate < butyl acetate, but for 3-methylbutyl-2-acetate the V^E values are intermediate to those of ethyl acetate or propyl acetate containing mixtures. With increasing temperature, the V^E values become more positive,

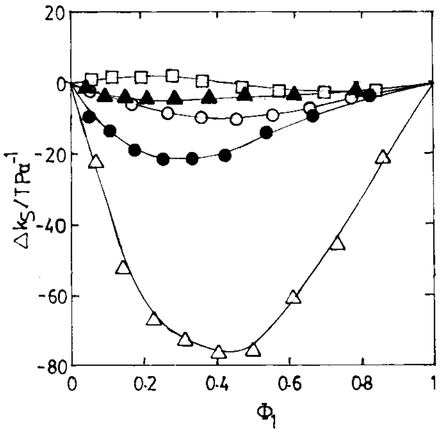

Figure 4. Plots of deviation in isentropic compressibility vs volume fraction of acrylonitrile at 298.15 K for the same mixtures given in Figure 1.

but these are not presented graphically to avoid the overcrowding. The V^E results of Haijun et al. (1994) at 298.15 K for the mixtures of acrylonitrile + aromatic hydrocarbon (benzene, toluene, *o*-, *m*-, and *p*-xylenes, ethylbenzene, or styrene) were also negative, further supporting higher specific interactions. On the other hand, for mixtures of acrylonitrile + *n*-alkanes (Sandhu and Singh, 1992), the V^E values are positive owing to weak dispersion type interactions.

The variation of $\Delta\eta$ with mole fraction, x_1, of acrylonitrile at 298.15 K displayed in Figure 2 is not very systematic. For acrylonitrile + methyl acetate, the $\Delta\eta$ values are positive over the entire composition range of the mixture. In the case of acrylonitrile + butyl acetate or + 3-methylbutyl-2-acetate, the $\Delta\eta$ vs x_1 curves are quite identical and vary in a sigmoidal manner owing to the varying interactions with composition of the mixture. On the other hand, for mixtures of ethyl acetate or propyl acetate with acrylonitrile, the opposite trends are observed; i.e., acrylonitrile + ethyl acetate mixture shows sigmoidal trends varying from negative to positive values, but a reverse is observed for acrylonitrile + propyl acetate mixture. Variations in $\Delta\eta$ curves at 303.15 and 308.15 K are almost identical to the curves presented at 298.15 K, but these are not displayed to avoid redundancy.

The plots of Δu vs x_1 at 298.15 K are displayed in Figure 3 wherein the Δu values are negative for acrylonitrile + propyl acetate, but for mixtures of acrylonitrile + ethyl acetate, a large positive Δu is observed. The values of Δu for the mixtures of acrylonitrile with methyl acetate or 3-methylbutyl-2-acetate are small and positive but vary almost identically. However, in the case of acrylonitrile + butyl acetate, the Δu values are positive and are nearly five times smaller than those values exhibited by acrylonitrile + ethyl acetate mixture.

The variation of Δk_S with volume fraction, ϕ_1, of acrylonitrile at 298.15 K is presented in Figure 4. A large negative Δk_S is observed for acrylonitrile + ethyl acetate mixture. In the case of acrylonitrile + butyl acetate mixture, the negative Δk_S values exhibit a slight sigmoidal trend. However, with acrylonitrile + methyl acetate or + 3-methylbutyl-2-acetate mixtures, the Δk_S values are negative, and these values are quite small without showing any clear-cut minima. For acrylonitrile + propyl acetate mixture, the Δk_S vs ϕ_1 curve follows slightly a sigmoidal trend with an inversion of sign at around $\phi_1 = 0.4$.

The results of ΔR vs ϕ_1 at 298.15 K presented in Figure 5 are negative for all the mixtures. These values show a

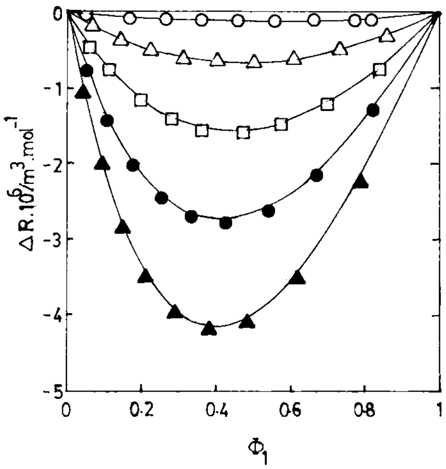

Figure 5. Plots of deviation in Lorenz–Lorentz molar refractivity vs volume fraction of acrylonitrile at 298.15 K for the same mixtures given in Figure 1.

systematic decrease from methyl acetate all the way to 3-methylbutyl-2-acetate, a behavior that is almost similar to V^E results. The ΔR vs ϕ_1 curves at 303.15 and 308.15 K show the same trends, but these are not presented. However, the effect of temperature on ΔR values is quite insignificant.

Conclusions

The physical properties for the mixtures presented here have not been studied in the earlier literature. Such a database will have importance in polyacrylonitrile processing industries because ultimately the properties of the polymer (polyacrylonitrile) depend on the interactions of the monomers (acrylonitrile) and the other molecules (esters) that are used as plasticizers. It is observed that the results of V^E, Δu, Δk_S, and ΔR show a systematic dependence on the size of the ester molecules, but not the $\Delta\eta$ values. The speed of sound values for acrylonitrile + 3-methylbutyl-2-acetate mixture do not show much variation with the composition of mixtures.

Literature Cited

Aminabhavi, T. M.; Bindu, G. Densities, Shear Viscosities, Refractive Indices, and Speeds of Sound of Bis(2-methoxyethyl) ether with Nonane, Decane, Dodecane, Tetradecane, and Hexadecane at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1994**, *39*, 529–534.

Aminabhavi, T. M.; Phayde H. T. S.; Khinnivar, R. S.; Bindu G. Densities, Refractive Indices, Speeds of Sound, and Viscosities of Diethylene Glycol Dimethyl Ether + Butyl Acetate at 298.15, 303.15, 308.15, 313.15, and 318.15 K. *J. Chem. Eng. Data* **1993**, *38*, 542–545.

Aralaguppi, M. I.; Aminabhavi, T. M.; Balundgi, R. H.; Joshi, S. S. Thermodynamic Interactions in Mixtures of Bromoform with Hydrocarbons. *J. Phys. Chem.* **1991**, *95*, 5299–5308.

Correa, A.; Blanco, A.; Tojo, J.; Correa, J. M.; Arce, A. Vapor–Liquid Equilibria of Pyridine + Acetate Mixtures at 101.325 kPa. *Collect. Czech. Chem. Commun.* **1991**, *56*, 2773–2785.

Haijun, W.; Guokang, Z.; Mingzhi, C. Excess volumes of (acrylonitrile + an aromatic hydrocarbon) at the temperature 298.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 457–460.

Marquardt, D. W. An Algorithm for Least-Squares Estimation of Nonlinear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431–441.

Ortega, J.; Matos, J. S.; Paz-Andrade, M. I.; Fernandez, J. Excess Molar Volumes of Ethyl Formate or Ethyl Acetate + 1- Chloroalkane at 298.15 K. *J. Chem. Eng. Data* **1987**, *32*, 464–466.

Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Techniques of Chemistry, Organic Solvents, Physical Properties and Methods of Purification*; John Wiley & Sons: New York, 1986; Vol. II.

Sandhu, J. S.; Singh, A. Excess molar volumes of (acrylonitrile + an *n*-alkan- 1-ol) at the temperature 298.15 K. *J. Chem. Thermodyn.* **1992**, *24*, 81–84.

Yoshikawa, H.; Kato, M. Vapor–Liquid Equilibria for Three Binary Systems Made of Methyl Ethyl Ketone with Acetone, Methyl Acetate, or *n*-Amyl Alcohol. *J. Chem. Eng. Data* **1991**, *36*, 57–60.

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