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Vapor−Liquid Equilibria and Excess Properties of the Binary System Vinyl Acetate + *p*-Xylene

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Isobaric vapor−liquid equilibria have been measured with a vapor recirculating type (modified Othmer's) equilibrium still for the system, vinyl acetate + *p*-xylene at 97.3 kPa. The system deviates positively from ideal behavior and does not have an azeotrope. The thermodynamic consistency of the experimental data was checked by Herington, Black, and Hirata tests. The activity coefficients were correlated by means of the Margules, Redlich−Kister, Black, and Wilson equations. A comparison of values of activity coefficients obtained by experimental data was made with UNIFAC model. Also the excess molar volumes, viscosities, and speeds of sound for the binary mixture at T = (303.15, 308.15, and 313.15) K have been determined for the whole compositional range. The deviations in viscosity and excess isentropic compressibility have also been estimated. All of the excess properties have been fitted to the Redlich−Kister equation.

Introduction

Thermodynamic and transport properties have been used as a qualitative and quantitative guide to understand the molecular interactions between the components of the mixture, to develop new theoretical models, and also to carry out engineering applications in the process industry. Data for these properties can be obtained experimentally or by using generalized methods that permit the calculation of the properties of mixtures. The development of a calculation method requires that an adequate database is available. Although many tabulated values of the above properties are generally available for the pure solvents, literature data for the various binary mixtures are often scarce. The present work aims to contribute to the development of a database for the vapor−liquid equilibria, excess molar volume, viscosity, and speed of sound of the binary mixture.

Vinyl acetate is a versatile and economically important chemical with a wide variety of industrial and commercial applications. It is used in the production of a wide range of polymers, which are used in the production of adhesives, paints, and food packing. *p*-Xylene is extensively used as a solvent, and it is also used in the synthesis of other compounds such as polyster resins and fibers, vitamins, and pharmaceutical products.

This work forms a part of continuing research[1,2] on the thermodynamic and thermophysical properties of binary mixtures containing a C_8 or C_9 hydrocarbon as one of the components. In this work, vapor−liquid equilibria have been measured for the system vinyl acetate + *p*-xylene at 97.3 kPa using a modified version of the recirculating type equilibrium still that was described earlier.[3,4] The system has a wide boiling range of 65.85 K and does not form an azeotrope.

Table 1. Physical Properties of the Pure Components at Different Temperatures

		$\rho \times 10^{-3}$/kg·m^{-3}		η/mPa·s	
component	T/K	exptl	lit	exptl	lit
vinyl acetate	303.15	0.9180	0.91820[15]	0.384	0.384[15]
	308.15	0.9042		0.361	
	313.15	0.8918		0.332	
p-xylene	303.15	0.8523	0.85230[16]	0.566	0.566[6]
	308.15	0.8479	0.84790[17]	0.537	0.539[17]
	313.15	0.8436	0.84364[18]	0.513	0.513[19]

Also in the present study, the experimental values of the excess molar volume, viscosity, and speed of sound at T = (303.15, 308.15, and 313.15) K for the system vinyl acetate + *p*-xylene have been determined over the entire compositional range. From the experimental data, densities, deviations in viscosity, and excess isentropic compressibility have been calculated. The densities and viscosities for this system at 298.15 K have already been reported earlier in the literature.[5]

Experimental Section

Chemicals. Vinyl acetate (S. D. Fine Chem. Ltd., India) and *p*-xylene (Riedel, Germany), AR grade, were purified using standard procedures[6] and stored over molecular sieves. The purity of the chemicals was checked by comparing the densities and viscosities with those reported in the literature as shown in Table 1.

Apparatus and Procedure. The vapor−liquid equilibrium data were obtained by using a modified version of the equilibrium still,[4] and a Bausch and Lomb Abbe-3L refractometer was used to analyze the equilibrated mixtures. The apparatus, modifications, and analytical techniques have already been described earlier.[7] The estimated uncertainties in the measurements of mole fraction were ± 0.0002, in temperature were ± 0.02 K, and in pressure were ± 0.27 kPa.

Excess molar volumes, which are reproducible to ± 0.003 cm^3·mol^{-1}, were measured with a continuous dilution dilatometer.[8] The density values have been estimated from the excess molar volume data with reproducibility better than ± 1 × 10^{-4}. Viscosities were measured with the help of modified Ubbelohde viscometer as described earlier.[9] The

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Table 2. Physical Constants of the Pure Components

constant	vinyl acetate	*p*-xylene
molecular wt	86.091[20]	106.169[20]
boiling point/K (at 101.3 kPa)	345.65[20]	411.501[20]
refractive index (at 298.15 K)	1.3934[20]	1.49325[20]
T_c/K	525.0[21]	616.2[21]
P_c/kPa	4348.9[21]	3509.1[21]
$V_c \times 10^6$/m^3·mol^{-1}	265.00[21]	379.00[21]
acentric factor, ω	0.3384[21]	0.32[21]
dipole moment, μ/D	1.79[21]	0[21]
Antoine constants, eq 4		
A	7.21010[22]	6.98820[22]
B	1296.130[22]	1451.792[22]
C	226.655[22]	215.111[22]

Table 3. Vapor−Liquid Equilibrium Data of Vinyl Acetate (1) + *p*-Xylene (2) System at 97.3 kPa

T/K	x_1	y_1	ln γ_1	ln γ_2
344.68	1.0000	1.0000	0.0000	0.5720
345.60	0.9850	0.9967	0.0000	0.5460
346.90	0.9550	0.9901	0.0001	0.5050
347.80	0.9250	0.9833	0.0002	0.4760
348.70	0.9000	0.9775	0.0003	0.4555
349.80	0.8450	0.9653	0.0003	0.4065
351.35	0.7635	0.9487	0.0090	0.3155
353.15	0.6455	0.9228	0.0936	0.2505
354.20	0.5948	0.9116	0.1316	0.2130
355.15	0.5379	0.8977	0.1883	0.1927
357.75	0.4390	0.8694	0.2828	0.1475
361.95	0.3120	0.8200	0.4449	0.1135
362.85	0.2954	0.8112	0.4633	0.1056
366.40	0.2330	0.7732	0.5539	0.0810
369.60	0.1850	0.7345	0.6464	0.0690
374.65	0.1394	0.6741	0.7100	0.0530
379.05	0.1096	0.6146	0.7461	0.0460
382.25	0.0914	0.5688	0.7711	0.0381
391.55	0.0496	0.4082	0.8291	0.0313
410.00	0.0000	0.0000	0.8680	0.0000

viscometer was calibrated at each temperature to determine the constants A and B:

$$\eta/\rho = At + B/t \tag{1}$$

where η is in mPa·s, ρ is in kg·m^{-3}, and t is in seconds.

The values of constants were obtained by measuring the flow time (t) with triple-distilled water and double-distilled benzene. The flow measurements were made with an electronic stopwatch with precision of ± 0.01 s. The reproducibility of viscosity results was found to be within ± 0.003 mPa·s. Speeds of sound were measured with an interferometer (UTI-101) with an uncertainty of ± 0.1 m·s^{-1}. The isentropic compressibility values estimated from the speed of sound data were within uncertainty of ± 0.2 T·Pa^{-1}. All the measurements were made at a constant temperature with the help of a circulating-type cryostat (type MK70, MLW, Germany) maintained at a temperature within ± 0.02 K.

Results and Correlations

The liquid-phase activity coefficients (γ) were calculated from the experimental data using the equations[10] below, which take into account the vapor-phase nonideality:

$$\gamma_1 = (Py_1/P_1^{\,0}x_1)\exp[(B_{11} - V_1)(P - P_1^{\,0})/RT + P\delta_{12}y_2^{\,2}/RT] \tag{2}$$

$$\gamma_2 = (Py_2/P_2^{\,0}x_2)\exp[(B_{22} - V_2)(P - P_2^{\,0})/RT + P\delta_{12}y_1^{\,2}/RT] \tag{3}$$

Table 4. Correlation Parameters for Activity Coefficient and Deviation in Vapor Phase Composition

correlations	A_1	A_2	A_3	deviation (Δy)
Margules	0.68116	0.58010	0.16188	0.0406
Redlich−Kister	0.59016	−0.05053	0.04047	0.0290
Black	0.64535	0.54370	0.03614	0.1066
Wilson	0.59255	0.85684		0.0279

Table 5. Excess Molar Volume (V^{E}), Viscosity (η), Speed of Sound (u), Density (ρ), and Compressibility (K_S) for *p*-Xylene (1) + Vinyl Acetate (2) System at Different Temperatures

x_1	$V^{\mathrm{E}} \times 10^6$ (m^3·mol^{-1})	η (mPa·s)	u (m·s^{-1})	$\rho \times 10^{-3}$ (kg·m^{-3})	K_S (T·Pa^{-1})
		T = 303.15 K			
1.0000	0.000	0.566	1283.7	0.8523	712.0
0.8654	0.006	0.538	1259.7	0.8591	733.5
0.7488	−0.004	0.512	1237.4	0.8656	754.5
0.6371	−0.027	0.489	1215.8	0.8722	775.6
0.5319	−0.051	0.469	1195.4	0.8789	796.2
0.4300	−0.061	0.453	1175.5	0.8856	817.5
0.3332	−0.072	0.440	1156.6	0.8924	837.7
0.2421	−0.073	0.428	1138.8	0.8991	857.9
0.1577	−0.068	0.415	1122.6	0.9055	876.3
0.0767	−0.043	0.400	1108.1	0.9119	893.1
0.0000	0.000	0.384	1095.9	0.9180	907.0
		T = 308.15 K			
1.0000	0.000	0.537	1271.0	0.8479	730.1
0.8654	0.044	0.504	1238.6	0.8535	763.7
0.7488	0.076	0.478	1211.9	0.8588	792.9
0.6371	0.092	0.453	1187.3	0.8642	820.9
0.5319	0.096	0.432	1165.3	0.8697	846.7
0.4300	0.089	0.414	1145.6	0.8754	870.4
0.3332	0.073	0.399	1128.0	0.8813	891.8
0.2421	0.057	0.387	1112.3	0.8871	911.1
0.1577	0.038	0.376	1098.2	0.8927	928.7
0.0767	0.020	0.367	1084.9	0.8985	945.6
0.0000	0.000	0.361	1072.5	0.9042	961.5
		T = 313.15K			
1.0000	0.000	0.513	1260.0	0.8436	746.6
0.8654	0.072	0.475	1224.5	0.8483	786.2
0.7488	0.113	0.447	1196.4	0.8527	819.3
0.6371	0.140	0.422	1171.0	0.8572	850.7
0.5319	0.148	0.399	1148.8	0.8619	879.1
0.4300	0.141	0.380	1128.6	0.8668	905.7
0.3332	0.121	0.365	1110.6	0.8718	930.0
0.2421	0.098	0.352	1094.7	0.8768	951.7
0.1577	0.072	0.341	1080.6	0.8817	971.2
0.0767	0.042	0.333	1067.7	0.8867	989.3
0.0000	0.000	0.332	1055.7	0.8918	1006.1

where x_1, x_2 and y_1, y_2 are the equilibrium mole fractions of components 1 and 2 in the liquid and vapor phases, respectively; T and P are the boiling point and the total pressure; V_1 and V_2 are the molar liquid volumes; B_{11} and B_{22} are the second virial coefficients of the pure components; B_{12} is the cross second virial coefficient; and

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}$$

The pure component vapor pressures (P^0) were calculated according to the Antoine equation:

$$\log(0.133\ P^0/\mathrm{kPa}) = A - [B/((C - 273.15) + (T/\mathrm{K}))] \tag{4}$$

where the constants A, B, and C are reported in Table 2.

The Lyckman et al.[11] correlation was used for the estimation of liquid molar volumes. The Pitzer and Curl equation modified by Tsonopoulos[12] was used in the evaluation of cross virial coefficients in this work.

The experimental values of excess volume (V^{E}), viscosity (η), and speed of sound (u) measured at different temperatures for the system are listed in Table 5.The density of

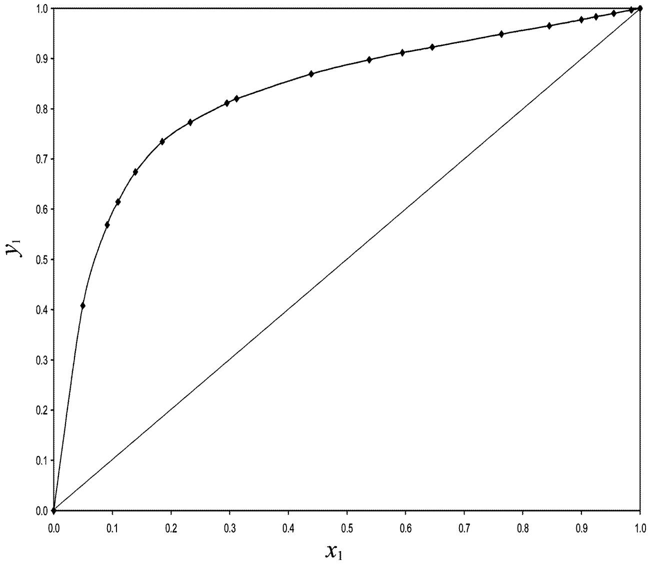

Figure 1. Plot of vapor−liquid equilibrium data for the system vinyl acetate (1) + *p*-xylene (2) at 97.3 kPa.

Table 6. Values of Coefficients of Redlich−Kister (eq 9) and Standard Deviations (eq 10)

T/K	A_0	A_1	A_2	A_3	A_4	σ
			$V^E \times 10^6/(m^3 \cdot mol^{-1})$			
303.15	−0.2149	0.3218	0.0756	0.1551	−0.2112	0.002
308.15	0.3775	0.1179	−0.0973	−0.0965	0.0275	0.001
313.15	0.5895	0.0955	−0.1612	−0.0962	0.2806	0.001
			$\Delta\eta/(mPa \cdot s)$			
303.15	−0.0445	−0.0451	0.1134	0.0189	−0.0758	0.0001
308.15	−0.0928	0.0156	0.0401	0.0018	−0.0587	0.0002
313.15	−0.1182	0.0150	0.0349	0.0216	−0.1309	0.0002
			$K_S^E/(T \cdot Pa^{-1})$			
303.15	−27.2847	−15.4924	14.6750	−28.4408	2.7543	0.04
308.15	33.8290	−8.4685	−28.7703	7.8921	20.2430	0.04
313.15	44.9290	−7.9306	−8.3467	8.2182	7.0138	0.06

the binary mixture was calculated from the excess molar volume data by the following relation:

$$\rho_m = (M_1x_1 + M_2x_2)/(V^E + x_1V_1^0 + x_2V_2^0) \qquad (5)$$

where x_1 and x_2 are mole fractions, M_1 and M_2 are molecular masses, and V_1^0 and V_2^0 are molar volumes of pure components 1 and 2, respectively.

The deviations in viscosity ($\Delta\eta$) were calculated by using

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \qquad (6)$$

where η_1 and η_2 are the viscosities of pure components 1 and 2, respectively, and η_m is the mixture viscosity.

The values of mixture density (ρ_m) and speed of sound (u) were used to calculate the isentropic compressibility (K_S) by using

$$K_S = u^{-2} \cdot \rho_m^{-1} \qquad (7)$$

The excess isentropic compressibility (K_S^E) was obtained from

$$K_S^E = K_S - (x_1K_{S_1} + x_2K_{S_2}) \qquad (8)$$

where K_{S_1} and K_{S_2} are isentropic compressibilities of pure components 1 and 2, respectively. The values of K_S are given in Table 5.

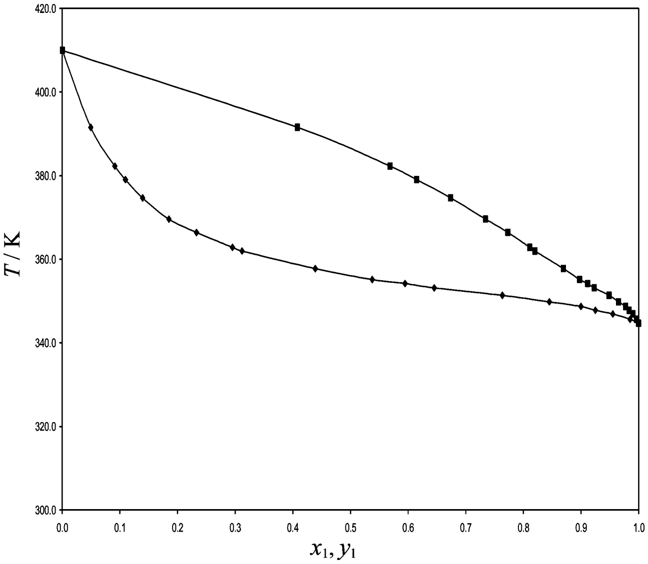

Figure 2. Plot of T vs x_1, y_1 data for the system vinyl acetate (1) + *p*-xylene (2).

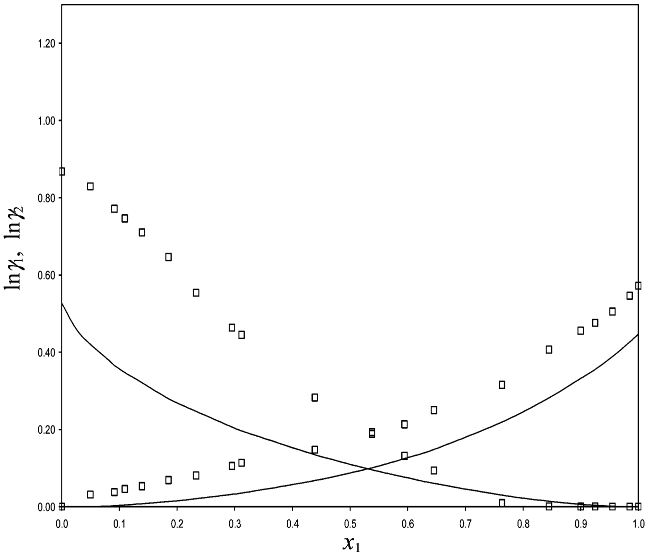

Figure 3. Plot of ln γ_1, ln γ_2 vs x_1 for the system vinyl acetate (1) + *p*-xylene (2) at 97.3 kPa: □, experimental; −, UNIFAC.

The excess volume (V^E), deviations in viscosity ($\Delta\eta$), and excess isentropic compressibility (K_S^E) were fitted to a Redlich−Kister[13] type equation:

$$A = x_1x_2\sum_{j=1}^{n} A_{j-1}(x_1 - x_2)^{(j-1)} \qquad (9)$$

where A is the property under consideration, A_{j-1} is the polynomial coefficient, and n is the polynomial degree.

The standard deviation in each case is calculated using

$$\sigma(X) = \left[\frac{\sum(X_{expt} - X_{calc})^2}{N - n}\right]^{1/2} \qquad (10)$$

where N is the number of data points, and n is the number of coefficients. The values of coefficients of eq 9 as determined by the method of least squares along with the standard deviations at different temperatures for the system are reported in Table 6.

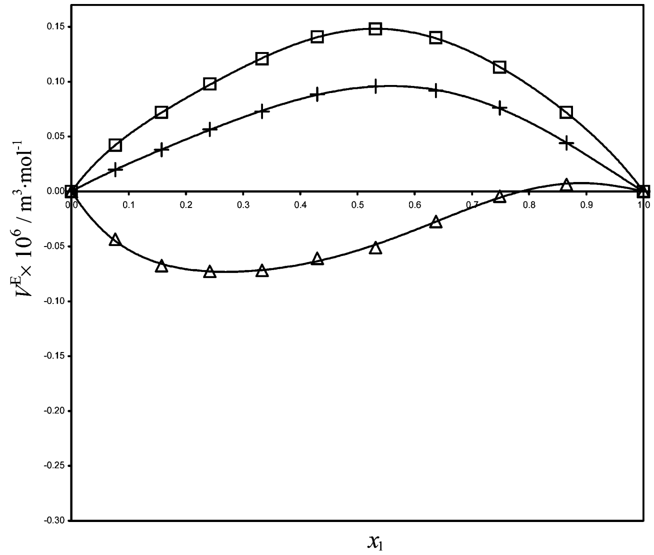

Figure 4. Excess molar volume (V^E) for the system *p*-xylene (1) + vinyl acetate (2) at △, 303.15 K; +, 308.15 K; and □, 313.15 K.

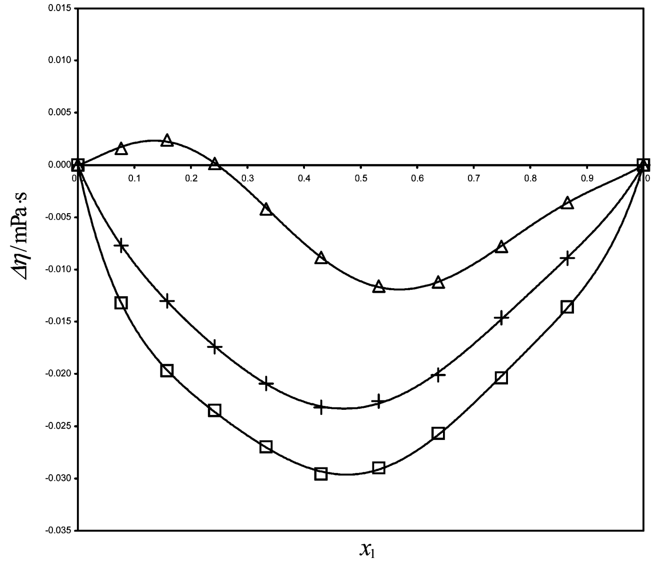

Figure 5. Viscosity deviations ($\Delta\eta$) for the system *p*-xylene (1) + vinyl acetate (2) at △, 303.15 K; +, 308.15 K; and □, 313.15 K.

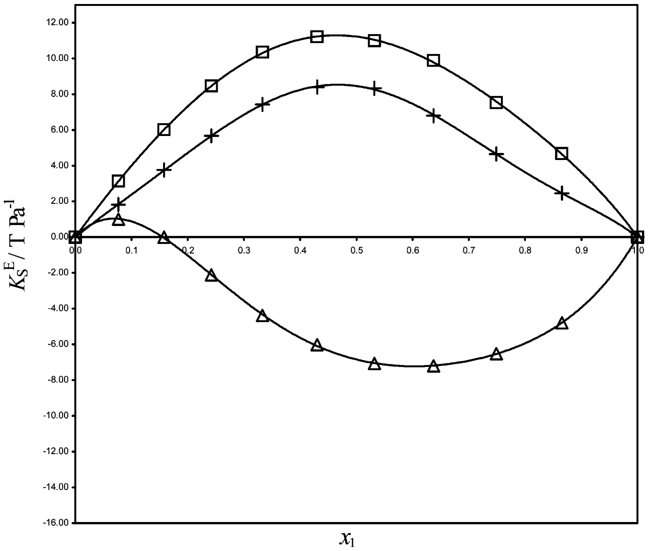

Figure 6. Excess compressibility (K_S^E) for the system *p*-xylene (1) + vinyl acetate (2) at △, 303.15 K; +, 308.15 K; and □, 313.15 K.

Discussion

Table 2 gives the physical constants of the pure components, and Table 3 gives the experimental T, x_1, y_1, and activity coefficients data. The x_1, y_1 and T, x_1, y_1 plots for vinyl acetate + *p*-xylene system at 97.3 kPa are given in Figures 1 and 2, respectively. Figure 3 gives the comparison of experimental activity coefficient data with those calculated using the UNIFAC model.[14] The data for the system were assessed for thermodynamic consistency by applying the Herington area test, Black test, and Hirata test and were found to be thermodynamically consistent.

From Table 4, it can be seen that the correlation of Margules, Redlich−Kister, and Wilson give much better fit as compared to the Black correlation with root-mean-square deviation in vapor-phase composition ranging from 0.0279 to 0.0406.

At 303.15 K, the sign inversion occurs from negative to positive at 0.78 mol fraction of *p*-xylene. V^E is negative, suggesting the presence of specific interactions. When the mole fraction of *p*-xylene increases, the dispersion forces become increasingly predominant over the specific interactions, thus exhibiting positive V^E. However, at 308.15 K and 313.15 K, the values of V^E are only positive.

At 303.15 K, the values of $\Delta\eta$ are positive up to 0.245 mol fraction of *p*-xylene and then become negative, whereas the values at 308.15 K and 313.15 K are only negative and more negative in the case of 313.15 K than 308.15 K.

It may be concluded that, at 303.15 K, negative V^E and positive $\Delta\eta$ indicate strong specific interactions through dipolar associations between the two types of components, whereas at 308.15 K and 313.15 K, the values of V^E are positive and $\Delta\eta$ are negative, indicating the predominance of the dispersion and dipolar forces over the specific interactions.

The same trend of V^E is followed in case of K_S^E, that a sign inversion takes place at 303.15 K; the values of K_S^E are positive at 308.15 K and 313.15 K.

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