Research Article

Thermo Physical Properties for Binary Mixture of Dimethylsulfoxide and Isopropylbenzene at Various Temperatures

Maninder Kumar and V. K. Rattan

University Institute of Chemical Engineering and Technology, Panjab University, Chandigarh 160014, India

Correspondence should be addressed to Maninder Kumar; maninderbhatoy@gmail.com

Density, refractive index, speed of sound, and viscosity have been measured of binary mixture dimethylsulfoxide (DMSO) + isopropylbenzene (CUMENE) over the whole composition range at 298.15, 303.15, 308.15, and 313.15 K and atmospheric pressure. From these experimental measurements the excess molar volume, deviations in viscosity, molar refractivity, speed of sound, and isentropic compressibility have been calculated. These deviations have been correlated by a polynomial Redlich-Kister equation to derive the coefficients and standard error. The viscosities have furthermore been correlated with two or three parameter models, that is, herric correlation and McAllister model, respectively.

1. Introduction

This paper contributes in part to our ongoing research on the solution properties. In the present study, data on density, viscosity, refractive index and speed of sound of binary mixture dimethylsulfoxide (DMSO) + isopropylbenzene at 298.15, 303.15, 308.15, and 313.15 K have been measured experimentally. From these results the excess molar volumes, viscosity deviations, and deviations in molar refraction and isentropic compressibility have been derived. Dimethylsulfoxide is a versatile nonaqueous dipolar aprotic solvent having wide range of applications. It is used as a solvent in many nucleophilic substitutions reactions. It has the ability to pass through membranes, an ability that has been verified by numerous subsequent researchers. It can penetrate through living tissues without damaging them. Therefore local anesthetic or penicillin can be carried through the skin without using a needle which makes it a paramount in medicinal field.

Isopropylbenzene is a naturally occurring substance present in coal tar and petroleum, insoluble in water, but is soluble in many organic solvents. It is used as a feedback for the production of Phenol and its coproduct acetone. It is also used as a solvent for fats and raisins.

The study of the thermodynamic properties of DMSO + isopropylbenzene mixtures is of interest in industrial fields where solvent mixtures could be used as selective solvents for numerous reactions.

2. Experimental Section

2.1. Materials. The chemicals used are of AR grade, dimethylsulfoxide (DMSO) and isopropylbenzene (CUMENE) are from Riedel, Germany. The chemicals are purified using standard procedure [1] and are stored over molecular sieves. The purity of the chemicals was verified by comparing viscosity, density, and refractive index with the known values reported in the literature as shown in Table 1. All the compositions are prepared by using SARTOIS balance. The possible error in the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$.

2.2. Density and Speed of Sound. Density and Speed of sound were measured by ANTON PAAR densimeter (DSA 5000) to

TABLE 1: Physical properties of components at 298.15 K.

| Component | T/K | ρ/g·cm^{-3} | | η/mPa·s | | n_D | |
		exptl	lit	exptl	lit	exptl	lit
DMSO	298.15	1.0940	1.09537[9]	1.9834	1.9910[9]	1.4798	1.4775[9]
CUMENE	298.15	0.8581	0.85743[9]	0.7388	0.7390[9]	1.4928	1.4889[9]

an accuracy of ±0.000005 g/cm^{-3} and ±0.5 m/s, respectively. The densimeter was calibrated with bi-distilled degassed water.

2.3. Viscosity.

Viscosities were measured by using calibrated modified Ubbelohde viscometer [2] as described earlier. The calibration of viscometer was done at each temperature in order to determine constants A and B of equation

$$\nu = \frac{\eta}{\rho} = At + \frac{B}{t}. \tag{1}$$

Flow time was measured with an electronic stop watch with precision of ±0.01 s. For each measurement viscometer was kept vertically in water bath for half an hour at constant temperature in order to attain thermodynamic equilibrium. The temperature of the bath was maintained constant with the help of circulating type cryostat where the temperature is controlled to ±0.02 K. The efflux time was repeated at least three times for each composition. The uncertainty in the values is within ±0.003 mPa·s.

2.4. Refractive Index.

Refractive indices were measured for sodium D-line by ABBE-3L refractometer having Bausch and Lomb lenses. The temperature was maintained constant with the water bath as described for the viscosity measurement. A minimum of three independent readings were taken for each composition, and the average value was considered in all the calculations. Refractive index data are accurate to ±0.0001 units.

3. Experimental Results and Correlations

At least three independent readings of all the physical property measurements on ρ, η, n_D, and u were taken for each composition and the averages of these experimental values are presented in Table 2. The experimentally determined values are used for the deviation calculations.

3.1. Excess Molar Volume.

Density is used to evaluate excess molar volume calculated by the equation

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2}, \tag{2}$$

where ρ_1, ρ_2 are the densities of pure components and ρ is the density of mixture. M_1, M_2 are the molecular weight of the two components. x_1, x_2 are the mole fraction of DMSO.

Excess gibb's free energy of activation has been also calculated using the viscosity and density of the mixture by the equation

$$\Delta G^E = RT \left[\ln (\eta V) - \sum_{i=1}^{2} x_i \ln (\eta_i V_i) \right] \tag{3}$$

R is a universal gas constant; T is the temperature of the mixture. η, η_i are the viscosity of the mixture and pure compound, respectively. V, V_i refers to the molar volume of the mixture and pure components, respectively.

3.2. Viscosity Calculations.

The deviation in viscosity is obtained by equation

$$\Delta \eta = \eta - x_1 \eta_1 - x_2 \eta_2. \tag{4}$$

η_1, η_2 refers to the viscosity of pure components and η is the viscosity of mixture. McAllister [3] model

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3x_1^2 x_2 \ln \eta_{12} + 3x_1 x_2^2 \ln \eta_{21}$$
$$- \ln \left[x_1 + x_2 \frac{M_2}{M_1} \right] + 3x_1^2 x_2 \ln \left[\frac{2 + (M_2/M_1)}{3} \right]$$
$$+ 3x_1 x_2^2 \ln \left[\frac{1 + (2M_2/M_1)}{3} \right] + x_2^3 \ln \left[\frac{M_2}{M_1} \right] \tag{5}$$

and herric correlation

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 x_2 \left[\alpha_{12} + \alpha'_{12} (x_1 - x_2) \right]$$
$$- \ln M_{\text{mix}} + x_1 \ln M_1 + x_2 \ln M_2 \tag{6}$$

have been fitted to viscosity data and it was found that both have the same standard errors at each temperature.

3.3. Isentropic Compressibility.

The experimental results for the speed of sound of binary mixture are listed in Table 2. The isentropic compressibility was evaluated by $K_S = u^{-2}\rho^{-1}$ and the deviation in isentropic compressibility is calculated using the below equation:

$$K_S^E = K_S - K_S^{id} \tag{7}$$

and deviation in speed of sound by

$$\Delta u = u - x_1 u_1 - x_2 u_2, \tag{8}$$

TABLE 2: Density, ρ, viscosity, η, speed of Sound, u, and refractive indices, n_D, for DMSO(1) + CUMENE(2) at different temperatures.

x_1	ρ g·cm^{-3}	η mPa·s	u m·s^{-1}	n_D
		Dimethylsulfoxide(1) + isopropylbenzene(2)		
		298.15 K		
0.0000	0.8581	0.7388	1325	1.4928
0.1047	0.8721	0.8025	1336	1.4918
0.1866	0.8842	0.8603	1348	1.4909
0.3013	0.9031	0.9610	1365	1.4897
0.3835	0.9180	1.0397	1378	1.4887
0.5032	0.9421	1.1661	1400	1.4871
0.5858	0.9610	1.2692	1417	1.4859
0.6972	0.9895	1.4337	1442	1.4841
0.7926	1.0178	1.5896	1467	1.4829
0.8929	1.0519	1.7648	1493	1.4811
1.0000	1.0940	1.9834	1523	1.4798
		303.15 K		
0.0000	0.8538	0.6806	1313	1.4915
0.1047	0.8676	0.7519	1327	1.4905
0.1866	0.8797	0.8143	1339	1.4898
0.3013	0.8984	0.9064	1356	1.4885
0.3835	0.9132	0.9814	1369	1.4875
0.5032	0.9372	1.1086	1391	1.4859
0.5858	0.9559	1.2075	1408	1.4848
0.6972	0.9843	1.3691	1434	1.4829
0.7926	1.0122	1.5230	1459	1.4815
0.8929	1.0459	1.6943	1485	1.4796
1.0000	1.0890	1.8949	1512	1.4781
		308.15 K		
0.0000	0.8495	0.6167	1301	1.4896
0.1047	0.8632	0.6962	1317	1.4888
0.1866	0.8751	0.7616	1329	1.4881
0.3013	0.8936	0.8565	1346	1.4869
0.3835	0.9083	0.9294	1359	1.4859
0.5032	0.9322	1.0493	1381	1.4844
0.5858	0.9508	1.1459	1398	1.4833
0.6972	0.9788	1.3059	1425	1.4814
0.7926	1.0064	1.4565	1449	1.4799
0.8929	1.0404	1.6131	1473	1.4784
1.0000	1.0840	1.7979	1498	1.4765
		313.15 K		
0.0000	0.8452	0.5588	1289	1.4871
0.1047	0.8587	0.6434	1306	1.4864
0.1866	0.8705	0.7103	1319	1.4857
0.3013	0.8887	0.8063	1337	1.4846
0.3835	0.9033	0.8756	1349	1.4836
0.5032	0.9270	0.9947	1372	1.4821
0.5858	0.9454	1.0872	1389	1.4809
0.6972	0.9732	1.2459	1416	1.4792
0.7926	1.0008	1.3888	1439	1.4778
0.8929	1.0348	1.5402	1462	1.4762
1.0000	1.0786	1.7054	1486	1.4742

TABLE 3: Derived parameters of Redlich-Kister equation (12) and standard deviation (13) for various functions of the binary mixtures at different temperatures.

T/K	A_0	A_1	A_2	A_3	σ
			V^E/cm^3·mol^{-1}		
298.15	−1.6771	−0.2071	−0.0446	−0.6836	0.00561
303.15	−1.5289	−0.2059	0.5117	−0.0903	0.0055
308.15	−1.3339	−0.0698	0.7925	0.1613	0.0046
313.15	−1.0884	0.0276	0.8186	0.1259	0.00549
			$\Delta\eta$/mPa·s		
298.15	−0.7847	−0.1293	0.0065	0.0645	0.00296
303.15	−0.7328	−0.1197	0.1384	0.0587	0.00178
308.15	−0.6393	−0.1245	0.2208	0.0967	0.00359
313.15	−0.5606	−0.1118	0.2922	0.141	0.00333
			K_S^E/TPa^{-1}		
298.15	−121.777	−64.3513	−24.8534	−29.8607	0.37123
303.15	−133.145	−66.2282	−46.6216	−17.4037	0.21847
308.15	−144.714	−73.4879	−59.3712	4.1751	0.27323
313.15	−157.833	−74.2561	−62.2923	10.1465	0.51612
			ΔR		
298.15	−0.7478	0.2009	−0.1111	0.2177	0.0089
303.15	−0.6486	0.1994	0.0606	0.045	0.0056
308.15	−0.5417	0.2093	0.2408	−0.0917	0.0127
313.15	−0.4454	0.1947	0.3148	−0.1187	0.0167
			ΔG^E/J·mol^{-1}		
298.15	133.9592	209.2619	16.9998	168.234	64.9657
303.15	246.905	198.0077	349.8235	15.7865	3.63471
308.15	488.086	69.5143	603.5378	59.8815	7.55398
313.15	724.2593	−0.9946	832.3713	64.9657	8.13559

where K_S^{id} stands for isentropic compressibility for an ideal mixture calculated using the relation

$$K_S^{id} = \sum_{i=1}^{2} \Phi_i \left[K_{S,i} + \frac{TV_i \left(a_i^2 \right)}{C_{p,i}} \right] - \left\{ \frac{T \left(\sum_{i=1}^{2} x_i V_i \right) \left(\sum_{i=1}^{2} \Phi_i a_i \right)^2}{\sum_{i=1}^{2} x_i C_{p,i}} \right\} \quad (9)$$

recommended by Kiyohara and Benson [4]. (1979) and Douhéret et al. [5] (1997), where a_i and $C_{p,i}$ are the volume expansion coefficient and heat capacity of the ith components.

3.4. Molar Refraction. Refractive indices have been used for the calculation of Molar refraction (R_m) obtained by using Lorenz-Lorenz [6] equation

$$R_m = \frac{\left[n_D^2 - 1 \right]}{\left[n_D^2 - 2 \right]} \sum \frac{x_i M_i}{\rho_m},$$

$$R_i = \frac{\left[n_D^2 - 1 \right]}{\left[n_D^2 - 2 \right]} \frac{M_i}{\rho_i}. \quad (10)$$

Deviation in molar refraction (ΔR) is calculated by equation

$$\Delta R = R_m - \sum \Phi_i R_i,$$

$$\Phi = \frac{x_i}{\sum x_j V_j}, \quad (11)$$

where n_D refers to refractive index, R_m is molar refraction of the mixture, R_i is molar refraction of the ith component, and Φ is ideal state volume fraction.

All the deviations (V^E, ΔR, $\Delta\eta$, Δu, K_S^E) have been fitted to Redlich-Kister [7] polynomial regression of the type

$$\Delta Y = x_1 x_2 \sum_{i=1}^{m} A_{j-1} \left(1 - 2x_1 \right)^{j-1} \quad (12)$$

to derive the constant A_j using the method of least square. Standard deviation for each case is calculated by

$$\sigma = \left[\frac{\sum \left(\Delta Y_{\text{expt}\,l} - \Delta Y_{\text{calc}\,d} \right)^2}{m - n} \right]^{0.5}, \quad (13)$$

where m is the number of data points and n is the number of coefficients. Derived parameters of the redlich-Kister (12) equation and standard deviations (13) are presented in Table 3

TABLE 4: Interaction parameters for the McAllister model (5) and herric correlation (6) for viscosity at different temperatures.
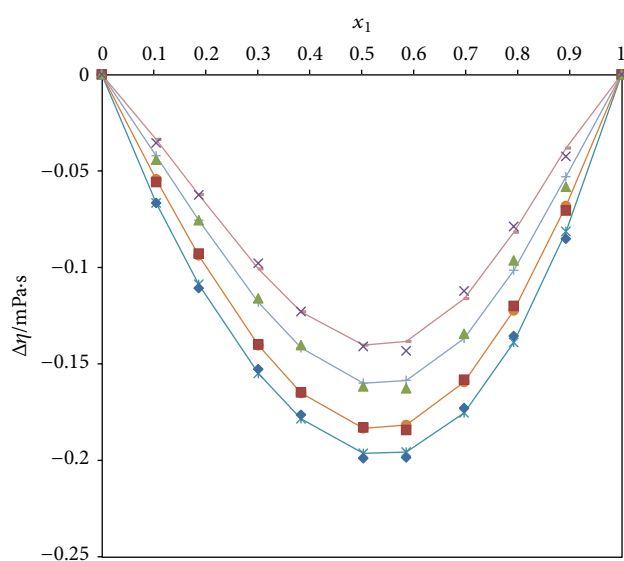
T/K	η_{12}	η_{21}	$\sigma(\eta)/mPa \cdot s$
	McAllister model		
298.15	0.975300	0.909494	0.00014
303.15	0.968905	0.905236	0.00032
308.15	0.962426	0.900935	0.00044
313.15	0.958670	0.900372	0.00051
T/K	α_{12}	α'_{12}	$\sigma(\eta)/mPa \cdot s$
	Herric correlation		
298.15	−0.02338	−0.01368	0.00014
303.15	−0.02600	−0.01677	0.00032
308.15	−0.02874	−0.01993	0.00044
313.15	−0.03047	−0.02084	0.00052
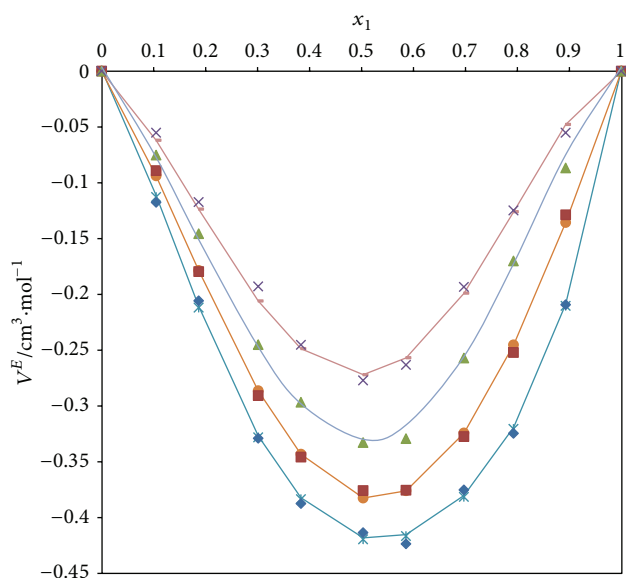
FIGURE 1: Experimental and calculated excess molar for the DMSO(1) + CUMENE(2) at ♦, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ×, 313.15 K; symbols represent the experimental values; lines are optimised by Redlich-Kister parameters.

FIGURE 2: Experimental and calculated deviations in viscosity for DMSO(1) + CUMENE(2) at ♦, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ×, 313.15 K; symbols represent the experimental values; lines are optimised by Redlich-Kister parameters.

4. Discussions

The deviations in excess molar volume at 298.15 to 313.15 K versus the mole fraction of DMSO are shown in Figure 1. The molar volume of the mixture and the viscosity data have also been used for the calculation of Gibb's free energy presented in Figure 5. The negative values of V^E indicate an interaction between the molecules which decreases with an increase of temperature. The large negative V^E values indicate a contraction of the volume and can be explained in terms of the heteroassociation in the mixture and suggest the strongest association occurs in this binary system [8].

The viscosity and deviations are presented in Table 2 and plotted in Figure 2, respectively. The negative values of $\Delta\eta$ obtained for the investigated mixture suggest that there may be reduction in the strength of H-bonds upon mixing. The

viscosity data can be qualitatively explained by considering that the Cumene has a branching CH_3 group, leading to packing of molecules in the pure state and a consequent lower density and larger mobility (lower viscosity) of the structure. This may be because interaction of Cumene with DMSO is less [6].

The viscosity data is also fitted to the two- and the three-parameter model, that is, herric correlation and the McAllister model and the evaluated parameters are presented in Table 4. The deviations decrease with the increase in temperature.

The deviations in molar refraction are shown in Figure 3. The ΔR values are negative for the whole composition range which goes on decreasing as the temperature of the solution increases.

The results of derived K_S^E are also plotted in Figure 4. The deviations are negative over the whole composition range.
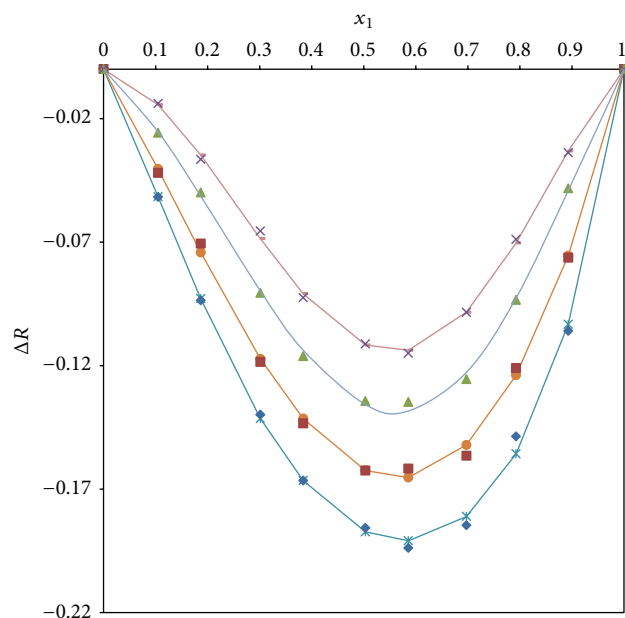
FIGURE 3: Experimental and calculated deviations in molar refraction for DMSO(1) + CUMENE(2) at ♦, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ×, 313.15 K; symbols represent the experimental values; lines are optimised by Redlich-Kister parameters.

FIGURE 5: Experimental and calculated deviations in Gibbs free energy of activation for DMSO(1) + CUMENE(2) at ♦, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ×, 313.15 K; symbols represent the experimental values; Lines are optimised by Redlich-Kister parameters.
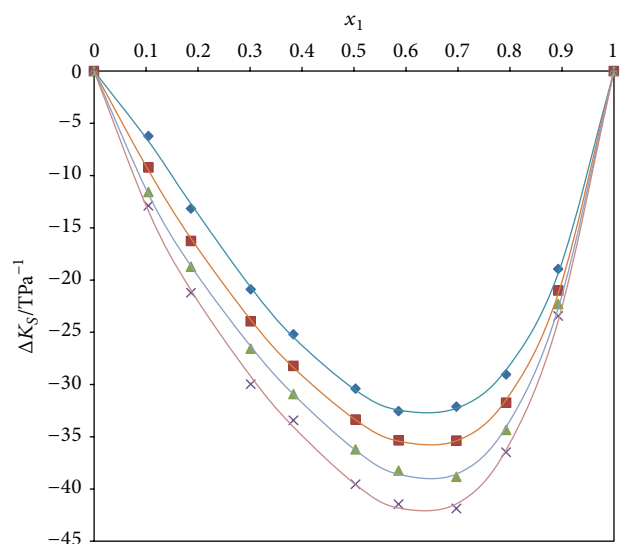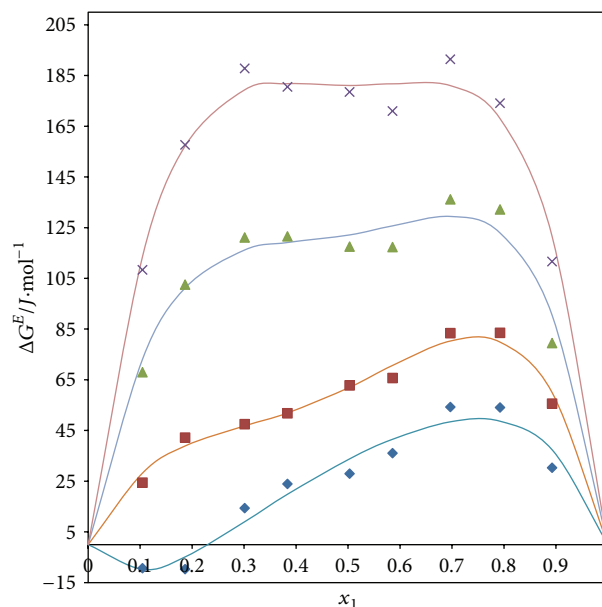

FIGURE 4: Experimental and calculated deviations in isentropic compressibility for DMSO(1) + CUMENE(2) at ♦, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ×, 313.15 K; symbols represent the experimental values; lines are optimised by Redlich-Kister parameters.

The K_S^E is negative near the composition of $x_1 = 0.7$ and then abruptly goes to zero.

Symbols

A_0, A_1, A_2, A_3:	Parameters of Redlich-Kister equation
A_{12}, A_{21}:	Interaction coefficient of McAllister model
$\alpha_{12}, \alpha_{12}'$:	Coefficients of Herric's correlation
v:	Kinematic viscosity (m^2/s)
ρ:	Density (g/cm^3)
σ:	Standard deviation
α:	Expansion coefficient
η:	Viscosity (cP)
ΔG^E:	Excess Gibbs free energy (J/mol)
V^E:	Excess molar volume
ΔK_S^E:	Excess isentropic compressibility
R:	Universal gas constant (8.314 J/mol.K)
T:	Absolute temperature (K)
Φ_i:	Volume fraction (dimensionless).

References

[1] J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents: Physical Properties and Methods of Purifications. Techniques of Chemistry*, vol. 2, John Wiley & Sons, New York, NY, USA, 1986.

[2] V. K. Rattan, S. Kapoor, and K. Tochigi, "Viscosities and densities of binary mixtures of toluene with acetic acid and propionic acid at (293.15, 303.15, 313.15, and 323.15) K," *Journal of Chemical and Engineering Data*, vol. 47, no. 5, pp. 1182–1184, 2002.

[3] R. A. McAllister, "The viscosity of liquid mixtures," *AIChE Journal*, vol. 6, pp. 427–431, 1960.

[4] D. Kiyohara and G. C. Benson, "Evaluation of excess isentropic compressibilities and isochoric heat capacities," *The Journal of Chemical Thermodynamics*, vol. 11, p. 861, 1979.

[5] G. Douhéret, M. I. Davis, I. J. Fjellanger, and H. Høiland, "Ultrasonic speeds and volumetric properties of binary mixtures of water with poly(ethylene glycol)s at 298.15 K," *Journal of the Chemical Society, Faraday Transactions*, vol. 93, no. 10, pp. 1943–1949, 1997.

[6] J. G. Baragi, M. I. Aralaguppi, T. M. Aminabhavi, M. Y. Kariduraganavar, and A. S. Kittur, "Density, viscosity, refractive index, and speed of sound for binary mixtures of anisole with 2-chloroethanol, 1,4-dioxane, tetrachloroethylene, tetrachloroethane, DMF, DMSO, and diethyl oxalate at (298.15, 303.15, and 308.15) K," *Journal of Chemical and Engineering Data*, vol. 50, no. 3, pp. 910–916, 2005.

[7] O. Redlich and A. T. Kister, "Algebraic representation of thermodynamic properties and the classification of solutions," *Industrial & Engineering Chemistry*, vol. 40, pp. 345–348, 1948.

[8] M. A. Saleh, M. Habibullah, M. Shamsuddin Ahmed et al., "Excess molar volumes and viscosities of some alkanols with cumene," *Physics and Chemistry of Liquids*, vol. 44, no. 1, pp. 31–43, 2006.

Journal of
Gravity

Journal of
Photonics

The Scientific
World Journal

Journal of
Soft Matter

Advances in
Condensed Matter Physics

Journal of
Fluids

Journal of
Aerodynamics

International Journal of
Statistical Mechanics

Hindawi

Submit your manuscripts at
http://www.hindawi.com

International Journal of
Optics

Journal of
Computational
Methods in Physics

Advances in
High Energy Physics

Journal of
Thermodynamics

Physics
Research International

Advances in
Astronomy

Journal of
Solid State Physics

Journal of
Astrophysics

International Journal of
Superconductivity

Journal of
Biophysics

Journal of
Atomic and
Molecular Physics