$\Delta \hat{S}^\circ$	standard entropy change of reaction, cal·mol^{-1}·K^{-1}
υ_i	stoichiometric coefficient of component *i*
φ_i	fugacity coefficient of component *i*

Subscripts

E	ETBE
Et	ethanol
e	equilibrium
f	formation
g	vapor phase
I	isobutene
i	component
N	nitrogen

Registry No. ETBE, 637-92-3; $(CH_3)_2C{=}CH_2$, 115-11-7; CH_3CH_2OH, 64-17-5.

Literature Cited

(1) Iborra, M.; Izquierdo, J. F.; Tejero, J.; Cunill, F. *CHEMTECH* **1988**, *18*, 120-2.
(2) Leum, L. N.; Macuga, J.; Kreps, S. I. U.S. Patent 2 480 940, 1949; *Chem. Abstr.* **1950**, *44*, 652.
(3) Macho, V.; Kavala, M.; Okresa, M.; Polievka, M. *Ropa Uhlie* **1982**, *24*, 397.
(4) Baratella, P.; Maiorano, G.; Schwarz, P.; Valtorta, L. Braz. Pedido PI BR 82 04 380, 1983; *Chem. Abstr.* **1983**, *98*, 197605.
(5) Lisichkin, G. V.; Kudryavtsev, G. V.; Bernadyuk, S. Z. *Zh. Vses. Khim. Ova* **1983**, *28*, 712-13.
(6) Childs, W. V. U.S. Patent 4 440 963, 1984; *Chem. Abstr.* **1984**, *100*, 209163.
(7) Staines, M. S. U.K. Patent Appl. GB. 2 123 411, 1984; *Chem. Abstr.* **1984**, *100*, 177611.
(8) Macho, V.; Vesely, V.; Baxa, J.; Truba, K.; Kavala, M.; Kordik, J.; Jureckous, E. Czech. Patent CS 229 708, 1986; *Chem. Abstr.* **1986**, *105*, 136893.
(9) Jones, E. M., Jr. U.S. Patent 4 504 687, 1985; *Chem. Abstr.* **1985**, *102*, 223213.
(10) Setinek, K.; Prokop, Z.; Kraus, M.; Zitny, Z. *Chem. Prum.* **1977**, *27*, 451-5.
(11) Fattore, V.; Massi Mauri, M.; Oriani, G.; Paret, G. *Hydrocarbon Process.* **1981**, *60*, 101-6.
(12) Cunill, F.; Tejero, J.; Izquierdo, J. F. *Appl. Catal.* **1987**, *34*, 341-51.
(13) Horsely, L. H. In *Azeotropic Data III*; Gould, R. F., Ed.; Advances in Chemistry Series 116; American Chemical Society: Washington DC, 1973; p 136.
(14) Evans, T. W.; Edlund, K. R. *Ind. Eng. Chem.* **1936**, *28*, 1186-8.
(15) Izquierdo, J. F.; Ferré, J.; Cunill, F. *Afinidad* **1987**, *44*, 419-23.
(16) Tejero, J.; Cunill, F.; Izquierdo, J. F. *Ind. Eng. Chem. Res.* **1988**, *27*, 338-43.
(17) Tejero, J. Ph.D. Thesis, University of Barcelona, 1986.
(18) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; Chapters 5 and 7.
(19) Hougen, O. A.; Watson, K. M.; Ragatz, R. A. *Chemical Process Principles Part II, Thermodynamics*, 2nd ed.; Wiley: New York, 1966; Chapter 25.
(20) Fenwick, J. O.; Harrop, D.; Head, A. J. *J. Chem. Thermodyn.* **1975**, *7*, 943-54.
(21) Perry, R. H.; Chilton, C. H., Eds.; *Chemical Engineer's Handbook*, 5th ed.; McGraw-Hill: New York, 1973; Chapter 4.
(22) Park, S. W.; Himmelblau, D. M. *AIChE J.* **1980**, *26*, 168-70.
(23) Hawes, R. W.; Kabel, R. L. *AIChE J.* **1968**, *14*, 606-11.

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Volumetric and Viscometric Studies of Binary Liquid Mixtures

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Density and viscosity measurements at 30 °C for the mixtures of *N*-methylaniline + 1,1,2,2-tetrachloroethane and *N*-methylaniline + dimethyl sulfoxide over the entire range of composition were used to calculate excess volume V^E, excess viscosity $\Delta\eta^E$, and excess molar Gibbs free energy of activation of flow $\delta(\Delta G^*)$. Grunberg and Nissan's parameter *d* was also calculated. The excess properties have been attributed to the molecular interaction between the dissimilar molecules of the liquid mixtures.

Introduction

In binary liquid mixtures, the molecular interaction between dissimilar molecules is influenced by structural arrangement along with shape and size of the molecules. The study of Fort and Moore (*1*) has revealed that the positive deviation in viscosity from ideal behavior arises from strong molecular interaction between dissimilar molecules, but if it is found to be negative, the dispersion forces are likely to dominate. The variation of viscosity and molar volume with changing composition of the mixtures has been investigated by various workers (*2-5*). This paper deals with our investigations of thermodynamic and transport properties of binary liquid mixtures and is in continuation of our previous studies (*6-8*). From the experimental results of densities and viscosities for the systems *N*-methylaniline + 1,1,2,2-tetrachloroethane and *N*-methylaniline + dimethyl sulfoxide (DMSO) at 30 °C, excess molar volume V^E, excess viscosity $\Delta\eta^E$, excess molar Gibbs free energy of activation of flow $\delta(\Delta G^*)$, and Grunberg and Nissan's parameter *d* have been computed.

Experimental Section

Materials. *N*-Methylaniline (Kotch-light), dimethyl sulfoxide (Riedel), and 1,1,2,2-tetrachloroethane (Riedel) were used after purification by the standard methods described by Weissberger (*9*). The calculated volumes of liquids were added to get mixtures of different known compositions. The mixtures were kept for 2 h, and then they were used for density and viscosity measurements.

Density Measurements. The densities of pure liquids and mixtures were determined by a double-armed pycnometer having capillaries of narrow bore provided with well-fitting glass stoppers in order to avoid changes in composition due to evaporation. The pycnometer was calibrated with double-distilled water and benzene. The accuracy in density was ±0.01%.

Viscosity Measurements. Viscosities were determined by a viscometer similar to the Cannon-Ubbehlohde viscometer, calibrated with benzene and toluene, and the accuracy in viscosity was ±0.005 cP.

Calculations

Molar volume *V* and viscosity η are calculated from the expressions

$$V = (X_1M_1 + X_2M_2)/\rho \tag{1}$$

$$\eta = \rho(at - b/t) \tag{2}$$

where M_1 and M_2 are molecular weights of the components 1 and 2 and X_1 and X_2 are their mole fractions, respectively. *t* is the time of flow in seconds, *a* and *b* are the constants of the viscometer, and ρ is density.

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Table I. Experimental Values of Density, ρ, Viscosity, η, and Allied Parameters for the System *N*-Methylaniline + 1,1,2,2-Tetrachloroethane at 30 °C

X_1[a]	ρ, g·cm^{-3}	V, mL·mol^{-1}	V^E, mL·mol^{-1}	η, cP	$\Delta\eta^E$, cP	d	$\delta(\Delta G^*)$, cal·mol^{-1}
0.0000	1.5795	106.274	0.000	1.381	0.000	0.00	0.00
0.1012	1.5168	106.617	+0.012	1.439	+0.021	+0.20	+10.84
0.1991	1.4565	106.951	+0.025	1.490	+0.036	+0.18	+17.70
0.3016	1.3941	107.276	+0.015	1.541	+0.049	+0.18	+23.07
0.4007	1.3350	107.519	−0.067	1.590	+0.061	+0.19	+27.46
0.5004	1.2753	107.807	−0.105	1.633	+0.067	+0.20	+29.09
0.6007	1.2154	108.110	−0.131	1.660	+0.057	+0.17	+24.48
0.7017	1.1552	108.437	−0.134	1.686	+0.046	+0.16	+19.15
0.7992	1.0972	108.776	−0.115	1.707	+0.031	+0.14	+13.06
0.9013	1.0367	109.145	−0.080	1.730	+0.016	+0.13	+6.65
1.0000	0.9782	109.548	0.000	1.751	0.000	0.00	0.00

[a] X_1 is mole fraction of *N*-methylaniline.

Table II. Experimental Values of Density, ρ, Viscosity, η, and Allied Parameters for the System *N*-Methylaniline + Dimethyl Sulfoxide at 30 °C

X_1[a]	ρ, g·cm^{-3}	V, mL·mol^{-1}	V^E, mL·mol^{-1}	η, cP	$\Delta\eta^E$, cP	d	$\delta(\Delta G^*)$, cal·mol^{-1}
0.0000	1.0905	71.646	0.000	1.803	0.000	0.00	0.00
0.1010	1.0734	75.519	+0.045	1.844	+0.047	+0.28	+21.12
0.2001	1.0589	79.270	+0.040	1.861	+0.069	+0.24	+32.52
0.3007	1.0456	83.071	+0.028	1.939	+0.152	+0.39	+61.38
0.3986	1.0340	86.752	−0.002	2.046	+0.264	+0.58	+96.56
0.4987	1.0230	90.525	−0.023	2.030	+0.313	+0.65	+111.14
0.6003	1.0131	94.321	−0.078	2.106	+0.335	+0.72	+116.40
0.6987	1.0043	97.992	−0.136	2.120	+0.354	+0.87	+119.95
0.8007	0.9950	101.646	−0.348	2.057	+0.296	+0.97	+99.39
0.9015	0.9860	105.781	−0.034	1.911	+0.155	+0.96	+55.33
1.0000	0.9782	109.548	0.000	1.751	0.000	0.00	0.00

[a] X_1 is mole fraction of *N*-methylaniline.

Excess molar volume, V^E, excess viscosity, $\Delta\eta^E$, and excess molar Gibbs free energy of activation of flow, $\delta(\Delta G^{\ddagger})$, are calculated by using the expressions

$$V^E = V_{mix} - (X_1V_1 + X_2V_2) \qquad (3)$$

$$\Delta\eta^E = \eta_{mix} - (X_1\eta_1 + X_2\eta_2) \qquad (4)$$

$$\delta(\Delta G^{\ddagger}) = RT[\ln \eta_{mix}V_{mix} - (X_1 \ln \eta_1V_1 + X_2 \ln \eta_2V_2)] \qquad (5)$$

Subscripts 1 and 2 refer to components 1 and 2; R is the gas constant and T is the temperature in absolute degrees.

Grunberg and Nissan's parameter, d (*10*), is calculated from the expression

$$\ln \eta_{mix} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1X_2d \qquad (6)$$

Each set of results was fitted with Redlich–Kister equation (*11*) of the form

$$A^E = X_1X_2[a_0 + a_1(X_1 - X_2) + a_2(X_1 - X_2)^2] \qquad (7)$$

where A^E represents excess functions under consideration and a_0, a_1, and a_2 are the coefficients of eq 7. The values of these coefficients for each function were determined by least-squares method for each set of liquid mixture. By substitution of these coefficients in eq 7, the calculated values of excess functions such as V^E, $\Delta\eta^E$, and $\delta(\Delta G^{\ddagger})$ were determined. The standard deviation (σ) has been calculated from the equation

$$\sigma = \left[\frac{\sum(A^E_{exptl} - A^E_{calcd})^2}{n - p}\right]^{1/2} \qquad (8)$$

where n is the number of measurements and p the number of coefficients.

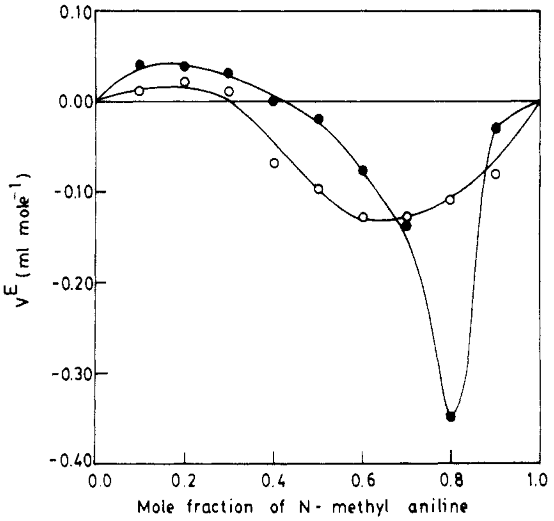

Figure 1. Excess molar volumes vs mole fraction of *N*-methylaniline for *N*-methylaniline + 1,1,2,2-tetrachloroethane (○) and *N*-methylaniline + dimethyl sulfoxide (●) at 30 °C.

Table III. Values of Coefficients of Eq 7 Determined by Least-Squares Method and Standard Deviation (σ)

system	function	a_0	a_1	a_2	σ
N-methylaniline + 1,1,2,2-tetrachloroethane	V^E	−0.3572	−0.6986	0.0424	0.017
	$\Delta\eta^E$	0.2463	−0.0283	−0.0781	0.002
	$\delta(\Delta G^*)$	107.63	−26.01	−22.53	1.102
N-methylaniline + dimethyl sulfoxide	V^E	−0.3179	−1.0565	0.0444	0.091
	$\Delta\eta^E$	1.2440	0.9494	−0.2071	0.021
	$\delta(\Delta G^*)$	439.33	288.12	−33.10	5.697

Results and Discussion

The experimental values of density, ρ, viscosity, η, and allied parameters for the two systems are given in Tables I and II. The coefficients a_0, a_1, and a_2 of eq 7 along with the standard deviation (σ) are given in Table III. The experimental values of V^E, $\Delta\eta^E$, and $\delta(\Delta G^{\ddagger})$ are plotted against the mole fraction of *N*-methylaniline, and the curves so obtained are shown in Figures 1, 2, and 3, respectively.

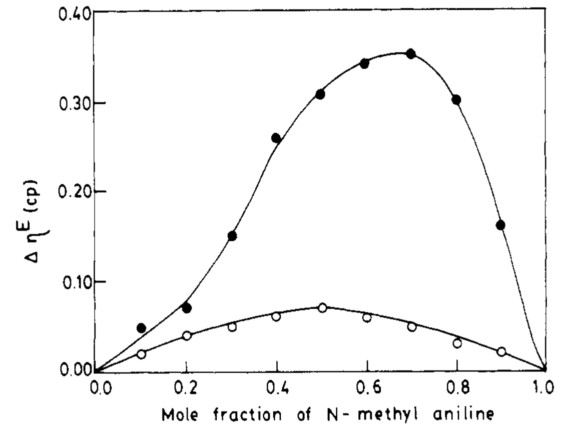

Figure 2. Excess viscosity vs mole fraction of *N*-methylaniline for *N*-methylaniline + 1,1,2,2-tetrachloroethane (O) and *N*-methylaniline + dimethyl sulfoxide (●) at 30 °C.

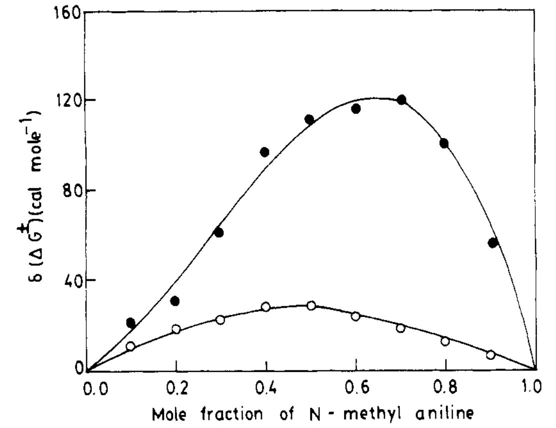

Figure 3. Excess molar Gibbs free energy of activation of flow vs mole fraction of *N*-methylaniline for *N*-methylaniline + 1,1,2,2-tetrachloroethane (O) and *N*-methylaniline + dimethyl sulfoxide (O) at 30 °C.

The negative values of excess molar volume, V^E, for the liquid systems are well explained by Prigogine (*12*) in terms of difference in size of the molecule or the dipole–dipole interaction between them leading to contraction in volume as compared to the ideal mixture. In the *N*-methylaniline + 1,1,2,2-tetrachloroethane system, at the lower fractions of *N*-methylaniline, the excess molar volume, V^E, is found to be positive (Figure 1), which may be attributed to the dissociation of *N*-methylaniline on addition of tetrachloroethane in excess. Above X = 0.2 mole fraction of *N*-methylaniline, the V^E tends to become increasingly negative. This contraction in volume may be ascribed to the closer approach of the dissimilar molecules due to electrostatic interactions, and possibly π-electron donor–acceptor complex formation occurs between the components of the mixture.

Attempts (*1*, *5*, *10*, *13–16*) have been made to explain the behavior of liquid mixtures on the basis of sign and magnitude of excess viscosity $\Delta\eta^E$, excess molar Gibbs free energy of activation of flow $\delta(\Delta G^\ddagger)$, and Nissan's parameter, *d*. The positive values of $\Delta\eta^E$, $\delta(\Delta G^\ddagger)$, and *d* indicate strong specific interaction whereas their negative values show weaker interaction.

For the system *N*-methylaniline + 1,1,2,2-tetrachloroethane, $\Delta\eta^E$ and $\delta(\Delta G^\ddagger)$ are positive over the entire composition range, further supporting the complex formation between the components of the mixture.

In case of the system *N*-methylaniline + dimethyl sulfoxide (DMSO), both the liquids are polar. There is evidence for the self-association of DMSO (*17*). As is evident from the Figure 1, for the mixtures of *N*-methylaniline + DMSO rich in DMSO, the excess molar volume V^E shows positive deviation, suggesting weak interaction between the dissimilar molecules. The positive deviations in V^E may be attributed to the dissociation of *N*-methylaniline molecules. As the concentration of *N*-methylaniline increases in the mixture, the deviations in V^E become increasingly negative with a well-marked minimum at X = 0.8 mole fraction of *N*-methylaniline demonstrating the complex formation.

Dielectric and refractive index studies of benzene + DMSO mixtures (*18*) have been discussed in terms of π-electron interaction. In the case of *N*-methylaniline, owing to increased electron density on aromatic ring, there is a greater possibility of π-electron complex formation between *N*-methylaniline + DMSO molecules. This contention is further supported by the positive values of $\Delta\eta^E$ and $\delta(\Delta G^\ddagger)$ (Figures 2 and 3) and Nissan's parameter, *d* (Table II).

Glossary

ρ	density
η	viscosity
V	molar volume
$\delta(\Delta G^\ddagger)$	excess molar Gibbs free energy of activation of flow
d	Grunberg and Nissan's parameter
σ	standard deviation
R	gas constant
T	absolute temperature
M	molecular weight

Subscripts

expti	experimental
calcd	calculated

Superscript

E	excess function

Registry No. DMSO, 67-68-5; *N*-methylaniline, 100-61-8; 1,1,2,2-tetrachloroethane, 79-34-5.

Literature Cited

(1) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* **1966**, *62*, 1112.
(2) Katz, M.; Lobo, P. W.; Minano, A. S.; Solimo, H. *Can. J. Chem.* **1971**, *49*, 2605.
(3) Solimo, H. O.; Riggo, R.; Davallo, F.; Katz, M. *Can. J. Chem.* **1973**, *53*, 1258.
(4) Brown, I.; Smith, F. *Aust. J. Chem.* **1962**, *15*, 1.
(5) Kumar, A.; Pitamber, N.; Prakash, S. *Indian J. Pure Appl. Phys.* **1984**, *22*, 608.
(6) Kumar, A.; Prakash, O.; Prakash, S. *J. Chem. Eng. Data* **1981**, *26*, 64.
(7) Prakash, O.; Sinha, S. *Acustica* **1984**, *54*, 223.
(8) Agnihotri, S. C.; Prakash, O. *Acoust. Lett.* **1985**, *9*, 27.
(9) Weissberger, A. *Techniques of Organic Chemistry*, 2nd ed.; Interscience: New York, 1955; Vol. VII.
(10) Grunberg, L.; Nissan, A. H. *Nature (London)* **1949**, *164*, 799.
(11) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 341.
(12) Prigogine, I. *The Molecular Theory of Solutions*; North Holland: Amsterdam, 1957.
(13) Prakash, S.; Sivanarayana, K.; Prakash, O. *Can. J. Chem.* **1980**, *58*, 942.
(14) Ramamoorthy, K. *Indian J. Pure Appl. Phys.* **1973**, *11*, 554.
(15) Nigam, R. K.; Singh, P. P. *Indian J. Chem.* **1971**, *9*, 691.
(16) Nigam, R. K.; Mahl, B. S. *Indian J. Chem.* **1971**, *9*, 1255.
(17) Drinkard, W.; Kivelson, D. *J. Phys. Chem.* **1958**, *62*, 1494.
(18) Lindberg, J. J.; Kenttama, J.; Nissema, A. *Suom. Kemistil. B* **1961**, *34*, 98, 156.

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