Excess Molar Volumes and Viscosities of Mixtures Containing Dimethylformamide (DMF) with benzene, o-xylene, 1, 4- Dioxane and Tetrahydrofuran at 298.15 K.

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Abstract

Measurements of excess molar volumes V^E , viscosities η , excess viscosities $\Delta \ln \eta$ and excess molar activation energies of viscous flow ΔG^E , are reported for binary mixtures of dimethylformamide (DMF) with , benzene , o-xylene , 1,4- dioxane and tetrahydrofuran are reported from density and viscosity measurements at 298.15 k and at atmospheric pressure over the entire composition range . The excess values are positive for the mixture (DMF+ polar solvent) and negative deviation from ideality for the mixture (DMF + non-polar solvent) over the whole composition range and discussed in the light of molecular interaction in the mixture.

Introduction

Obviously, the starting materials of many chemical products are aromatic compounds therefore the petroleum industry is interested in finding ways and means of extracting and recovering these aromatic compounds in pure form from oil. Consequently, wide research was carried out to find a solvent that is highly selective as well as maintaing sufficient solvent power to prevent the separation of phases during the extractive distillation process. Solvents that are highly polar with high boiling points possess such properties[1].

Dimethylformamide as pure solvent is certainly to some extent associated by means of nonspecific dipole-dipole interaction , and is of particular interest because any significant structural effects are absent due to the lack of hydrogen bonds ; therefore it may work as an aprotic protophilic solvent of large dipole moment and high dielectric constant (μ=3.24 D and ε=36.70 at 298.15 K) .It has been used in the separation of saturated and unsaturated hydrocarbons and serves as a solvent for many polymers [2-5]. The physical and thermodynamic properties of binary mixtures containing DMF as a common solvent with different organic liquids have been studied by many authors [6-11] . Although a large number of investigations are carried in liquid mixtures having DMF as one of the components , It is found that no work has been made so for to the description of the thermodynamic properties of (DMF + polar solvents) and (DMF + nonpolar solvents) .

In general, excess volume depends mainly on two effects: a) the variation of the intermolecular forces when two components come in to contact, and b) the variation of the molecular packing as a consequence of the differences in the size and shape of the molecules of the components [12-14].

Theoretical and experimental interest has increased in recent years in the thermodynamic properties of liquid mixtures containing associated compounds. The majority of the theoretical models, generally based on a rigid lattice concept, are not suitable for the prediction of volumetric properties such as V^E.Thus, the model of Nitta [15] permits the

prediction of several properties of pure compounds and mixtures, simultaneously, including V^E [16] . An ideal solution may be defined as one in which no specific forces of attractions exist between the components of solution and no change occur in the properties of the components when mixed. Thus in an ideal solution , the total solution volume equal to the sum of volumes of the components and the other physical properties such as refractive index , fluidity and vapor pressure can be calculated by taking the molal average of the components properties [17] . Thermodynamic and transport properties of binary and ternary mixtures with different organic liquids have been studied by many authors [18-20].

In this paper the experimental values of excess molar volumes , excess viscosities and excess molar activation energies for DMF + benzene ,+ o-xylene , + 1-4 dioxane and tetrahydrofuran at 298.15 K and at atmospheric pressure which are calculated from the density and viscosity measurements of binary liquid mixtures over the entire composition range are reported and has been used to obtain a complete picture of the volumetric and viscometric behaviour of dimethylformamide in polar and nonpolar solvents

Experimental

All the organic liquids used were of analar grade and obtained from BDH Chemicals .The density measurements for the pure components are summarized and compared with the corresponding literature values in Table I. Since the agreement is good, further purification of the employed compounds was not performed. The investigation of sources of errors in V^E by Lepory et.al., [21], showed namely, that purity of substances was not a crucial factor in V^E measurements.

The compositions of the binary mixtures were determined by weighing the appropriate amounts of the pure components with a Mettler mass balance with an accuracy $\pm 10^{-4}$ g, and stored them into suitably stoppered flasks in the dark at constant humidity and temperature in order to prevent the samples from preferential evaporation. The excess molar volumes were calculated from the densities of the pure liquids and mixtures. The densities were measured with the help of standard bicapillary pyknometer technique used by other workers [22].The pyknometer was self-filling in type and offers accuracy up to 1 to 4 parts in 10^4 , this pyknometer was immersed in the thermostatic bath maintained at 298.15 K .

The viscosities of the pure liquids and mixtures were determined by using a suspended-level Ubbelohde viscometer. An electronically operated constant temperature water bath is used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature in a bath controlled to ± 0.01 K at 298.15 K . The flow time was determined electronically by using an electronic timer with a precision ± 0.01 s. . Before each series of measurements , the instrument was calibrated with doubly distilled water and dry air at atmospheric pressure . The accuracy of the technique described was checked by measuring the V^E data for the test binary mixture benzene + cyclohexane at 298.15 K , which nearly ideal solutions has been used as reference system , the results agree satisfactorily with those of other authors.

Result and Discussion

The excess molar volumes V^E , excess viscosities $\Delta \ln \eta$ and molar excess Gibbs energies for the activation of viscous flow ΔG^E of the binary DMF + benzene ,+ o-xylene , + 1-4 dioxane and tetrahydrofuran mixtures were determined at 298.15 K. The excess molar volumes were calculated from the density measurements using the equation:

$$V^E (cm^3 \ mol^{-1}) = [(\ x_1 M_1 + x_2 M_2\ ) / \rho\ ] - [(x_1 M_1)/ \rho_1] - [(x_2 M_2) / \rho_2] \qquad (1)$$

Where x_1 and x_2 the mole fraction of the components , M_1 and M_2 represents the molar mass and ρ_1, ρ_2 stand for the densities of the pure components and the liquid mixture , respectively .The imprecision of the determination of the V^E is estimated to be less than 2×10^{-4} cm^3 mol^{-1} . The experimental values of V^E are given in Table 3 and presented graphically in Figs 1,2 .

Experimental viscosities η are listed in Table 3 . Excess molar viscosities $\Delta \ln \eta$ and excess molar activation energies ΔG^E were calculated from the following equations:

$$\Delta \ln \eta(cP) = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{2}$$

$$\Delta G^E (J.mol^{-1}) = RT [\ln \eta_m V_m - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \tag{3}$$

Where η_m and V_m are respectively of the viscosity and molar volume of the binary mixture, η_1 and V_1 represent the viscosity and molar volume of the component (x_1) DMF, η_2 and V_2 represent the viscosity and molar volume of pure liquids (benzene, o-xylene , 1,4- dioxane and tetrahydrofuran) (x_2) . T temperature (K), R gas constant. The obtained results of the experimental and calculated properties for the binary mixture are listed in table 3 and illustrated in Figs 3, 4 respectively over the whole mole fraction range.

The X^E properties (V^E, $\Delta \ln \eta$ and ΔG^E) were fitted to variable degree function using the Redlich-Kister equation [23]:

$$X^E = x_1 x_2 \Sigma A_i (x_1 - x_2) \tag{4}$$

Where x_1 (DMF) and x_2 (pure liquids) are the mole fraction. The n A_i coefficients were processed by unweighted least –squares fitting and are listed in Table 2 .

Volumetric behaviour

In order to understand more about the nature of interaction between the components of liquid mixtures, it is necessary to discuss the same in terms of excess parameters rather than actual values. They can yield an idea about the non linearity of the system as association or other type of interactions.

The excess molar volumes V^E for the binary mixtures (DMF+ benzene ,o-xylene) Fig. 1 were negative over the whole mole fraction range at 298.15 K. The polar molecule may associate with the non-polar solvent molecules it is proposed that the molecular association rise because of the interaction of the positive fractional charge at the sight of carbon atoms in DMF and π-delocalized electron cloud in the benzene ring of the benzene molecule [8]. The V^E values were positive for the binary mixtures (DMF + dioxane , tetrahydrofuran) (Fig.2) can be explained by the predominance of expansion in volume , caused by the loss of dipolar association and difference in size and shape of component molecules , over contraction in volumes , due to the dipole –dipole and dipole-induced dipole interactions .

Viscometric behaviour

The experimental data of the mixing viscosities and excess free energies are plotted in Figs.(3,4,5) as a function of the mole fraction x of a polar and nonpolar solvent . All mixtures deviate from ideality . The $\Delta \ln \eta$ (cP) values were negative deviation for all the mixtures in Fig. 3, this might reflect the effect of several factors, i.e. inductive, steric, geometrical and orientational disordered. The ΔG^E (J.mol^{-1}) values were positive for the mixtures (Fig. 4) often as a sign of strong association by H-bonding or as a singn of fitting of one molecule into the cavities of the other or as a consequence of both , the DMF molecules behave similarly if surrounded by 1,4- dioxane and tetrahydrofuran molecules or by other DMF molecules [24] Interaction between the carbonyl group in the N,N-dimethylforamide and the benzene ring is

greater than the dipole breaking interaction . Interaction of the dimethylforamide molecule with 1,4- dioxane and tetrahydrofuran molecules can occur through the free electron pair of the DMF oxygen atom only , since the electron pair on the nitrogen atom is protected by two methyl groups . Fig. (5) Shows negative deviation from ideality, negative values can be explained by the predominance of expansion in volume, caused by loss of dipolar association and difference in size and shape of component molecules, over contraction in volume, due to the dipole-dipole and dipole-induced dipole interaction . The $\Delta \ln \eta$ (cP) and ΔG^E (J.mol^{-1}) values determined at different compositions reflect the type of intermolecular interaction , and are approximately proportions to the extent of the interactions , these two magnitudes may also be considered as a reliable measure of the extant of the interaction between unlike molecules .

Conclusions

The excess molar volumes V^E , excess viscosities $\Delta \ln \eta$ and molar excess Gibbs energies for the activation of viscous flow ΔG^E for all binary mixtures studied are positive with (DMF + polar solvent), and negative with (DMF + non-polar solvent) over the whole mole fraction range . Such behaviors in these binary mixtures may arise due to dipole-dipole interaction and the polar nature of different molecular entities in the mixture.

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Table (I): Densities ρ (g.cm^{-3}) and viscosities (cP), of the pure component liquids used in this   wok, measured at 298.15 K.

Component	ρ (g.cm^3)		η (cP)	
	Obs.	Lit.	Obs.	Lit.
Benzene	0.78447	0.78452[a]	0.611	0.599[a]
o-Xylene	0.89705	0.89714[a]	0.832	0.811[a]
1,4- Dioxane	1.03014	1.03008[b]	1.083	1.087[c]
Tetrahydrofuran	0.88596	0.88591[b]	0.456	0.451[c]
DMF	0.9213	0.92230	0.900	0.920[c]

(a) = [20]   (b)= [21]   (c)= [22]

Table (2): Coefficients A_i of eq. [4] and standard deviations SD in cm^3.

mol^{-1} for binary systems

Mixture	A_0	A_1	A_2	A_3	SD
DMF+Benzene	0.781	-0.8382	0.8941	2.095	0.0007
DMF+o-Xylene	0.653	-0.4563	0.4753	1.678	0.0002
DMF+ 1-4 Dioxane	0.342	2.9540	3.8760	1.043	0.0003
DMF+Tetrahydrofuran	1.103	-0.4350	0.5620	2.851	0.0008

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Table(3): Excess molar volumes V^E , viscosities η , excess viscosities Δ ln η and excess molar activation energies of viscous flow ΔG^E of x DMF + (1-x) (Benzene , o-xylene , 1-4 Dioxane and Tetrahydrofuran) at 298.15 K.

X	V^E (cm^3 mol^{-1})	η(cP)	$\Delta \ln \eta$ (cP)	ΔG^E (J.mol^{-1})
		xDMF + (1-x) benzene at 298.15K		
0.0000	0.0000	10.018	0.0000	0.00
0.03817	-0.1391	9.819	-0.0201	-82
0.11354	-0.3748	8.120	-0.0652	-198
0.24118	-0.5918	7.653	-0.0891	-300
0.32218	-0.7135	6.901	-0.121	-374
0.45213	-0.8965	5.452	-0.152	-402
0.5212	-1.0539	4.653	-0.159	-436
0.59987	-1.1412	3.379	-0.132	-442
0.6895	-1.0972	2.438	-0.112	-380
0.74581	-0.9954	1.217	-0.0789	-325
0.82541	-0.7945	0.963	-0.0648	-275
0.89632	-0.6682	0.791	-0.0432	-228
0.98152	-0.2852	0.579	-0.0106	-56
1.0000	0.0000	0.0000	0.0000	0.00
		xDMF + (1-x) o-xylene at 298.15		
0.0000	0.0000	9.871	0.0000	0.00
0.05693	-0.2452	7.991	-0.0452	-156
0.09896	-0.4512	6.841	-0.0699	-200
0.18962	-0.7825	5.783	-0.0932	-380
0.29654	-0.9996	4.863	-0.123	-476
0.38411	-1.2996	3.874	-0.1461	-596
0.47581	-1.4521	2.986	-0.182	-662
0.55412	-1.6451	1.975	-0.192	-631
0.65432	-1.8364	0.987	-0.179	-587
0.73215	-1.9912	0.842	-0.132	-432
0.82132	-1.73	0.783	-0.084	-384
0.89991	-0.932	0.687	-0.063	-299
0.95891	-0.59	0.601	-0.0321	-88
1.0000	0.00	0.00	0.000	0.00
		xDMF + (1-x) 1-4 dioxane at 298.15		
0.0000	0.0000	10.941	0.0000	0.00
0.11254	0.0755	9.741	-0.0221	-94
0.17432	0.0899	8.941	-0.0253	-245
0.22987	0.1085	7.541	-0.0281	-394
0.29635	0.1524	6.031	-0.0423	-468
0.33544	0.1653	5.721	-0.0545	-686
0.41257	0.1763	4.910	-0.0668	-761
0.49856	0.1632	3.873	-0.0546	-783
0.56423	0.1582	2.543	-0.0451	-728
0.63513	0.1421	1.328	-0.0301	-628
0.75623	0.1256	0.952	-0.0278	-542
0.84236	0.1058	0.701	-0.0121	-434
0.95623	0.021	0.682	-0.005	-112
1.0000	0.0000	0.0000	0.0000	0.00
		xDMF + (1-x) tetrahydrofuran at 298.15		
0.0000	0.0000	10.051	0.0000	0.00
0.11211	0.0958	9.042	-0.0318	-27
0.19845	0.1218	8.964	-0.0431	-138
0.25812	0.1601	7.976	-0.0525	-295
0.32115	0.1893	6.552	-0.0673	-382
0.41265	0.2128	5.644	-0.0837	-496
0.49625	0.2317	4.432	-0.0942	-677
0.52418	0.2291	3.651	-0.0879	-680
0.63213	0.1972	2.986	-0.0600	-556
0.78412	0.165	1.032	-0.0364	-460
0.85413	0.100	0.981	-0.0247	-321
0.95324	0.0798	0.854	-0.0156	-165
0.98926	0.0122	0.701	-0.004	-30
1.0000	0.000	0.000	0.0000	0.00

X_1
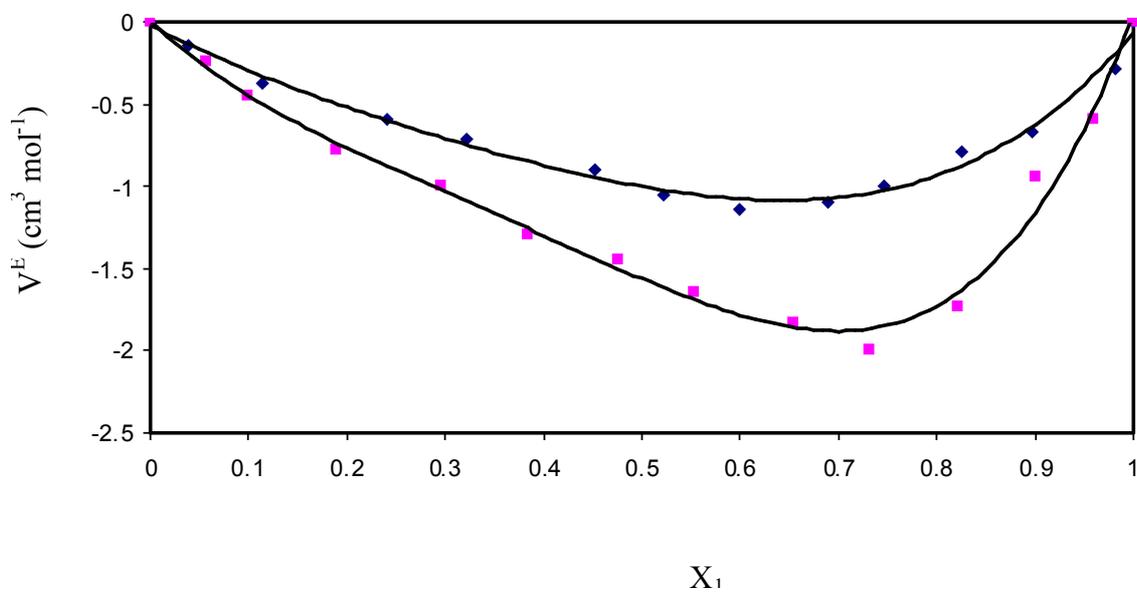
Fig.(1) Excess molar volumes, for x an DMF + (1-x) benzene (♦); o-xylene (■) at 298.15 K.
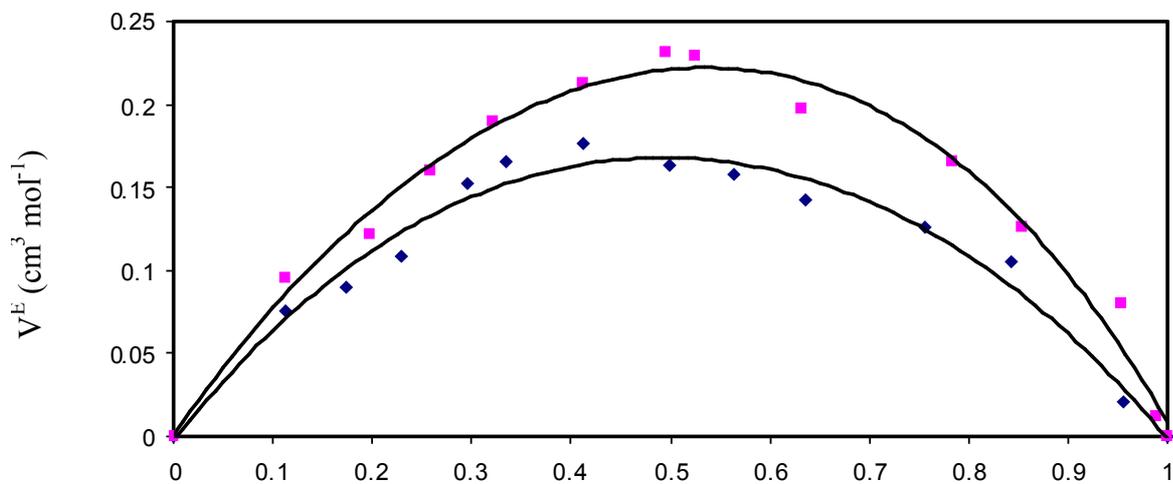
Fig. (2) Excess molar volumes, for x an D X_1 **1-x) 1-4 Dioxane (♦); Tetrahydrofuran (■)at 298.15 K.**
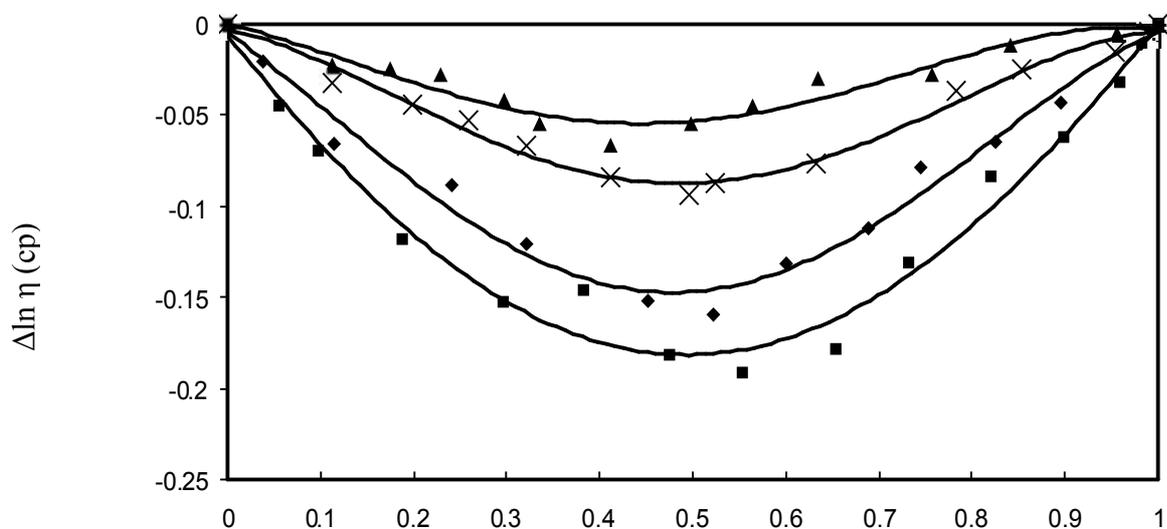
Fig.(3) Excess molar viscosities $\Delta \ln \eta(cP)$ for x an DMF + (1-x) benzene (■) , o-xylene (♦) , 1,4- Dioxane (x) , and Tetrahydrofuran (▲) at 298.15 K .
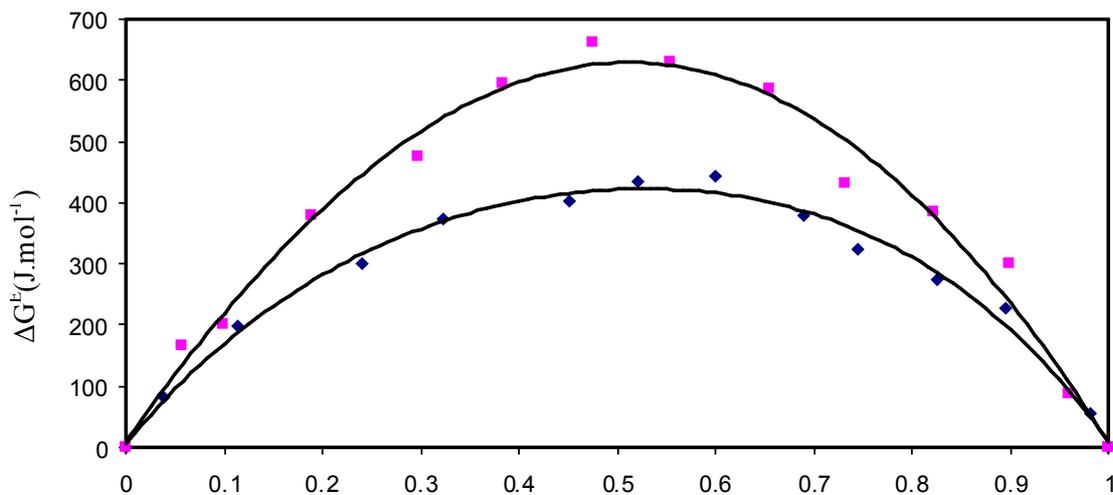
Fig.(4) Excess molar Gibbs free energy of activation of viscous flow, ΔG^{E} for x an DM (1-x) 1-4,Dioxane (♦); Tetrahydrofuran (■) at 298.15 K.
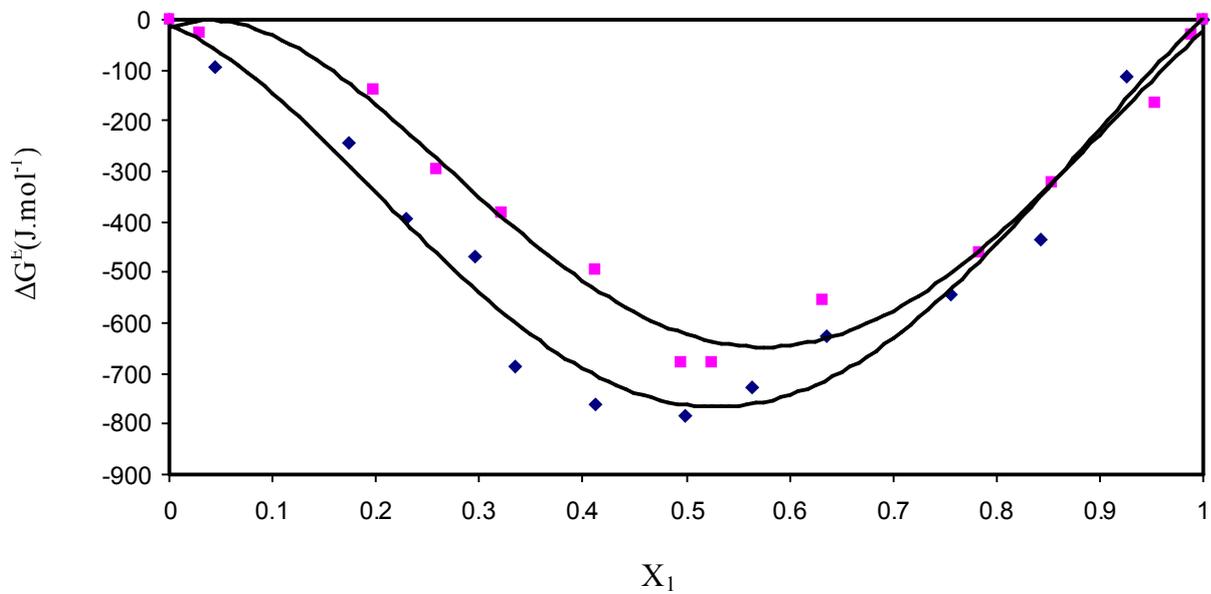
Fig. (5) Excess molar Gibbs free energy of activation of viscous flow, ΔG^E for x an DMF+(1-x) benzene1-4 Dioxane (♦); o-xylene (■) at 298.15 K .

الحجوم المولية الفا ئضة واللزوجة للمخاليط الثنائية للدايمثيل فورامايد مع البنزين ،اورثوزايلين، 4,1– دايوكسان وتيترايهيدروفيوران عند درجة 298.15 مطلقة

عباس عبدالامير كاظم

قسم الكيمياء ، كلية التربية ،جامعة القادسية

الخلاصة

تم في هذا البحث قياس كل من الكثافة واللزوجة لمخاليط مختلفة من دايمثيل فورم امايد مع البنزين والورثوزايلين و1,4 داي اوكسان والتتراهيدروفيوران في درجة حرارة 298.15 مطلقة . كما حسبت الحجوم الفائضة ، واللزوجة الفائضة وطاقة التنشيط الفائضة من الكثافة واللزوجة التي تم قيست عمليا للمذيبات النقية ومخاليطها . تبين من النتائج التي تم الحصول عليها في هذا البحث أن هناك حيوداً عن المثالية بالاتجاه الموجب في مخاليط داي مثيل فورم اميد   مع المذيبات القطبية وحيودا عن المثالية بالاتجاه السالب في مخاليط داي مثيل فورم اميد مع المذييات   اللاقطبية وقد تم تفسير ذلك في ضوء التداخلات الجزيئية بين جزيئات المذيبات في المزيج .