

Excess Molar Volumes and Viscosities of Binary Mixtures of an Aromatic Hydrocarbon and Sulfolane at 298.15 K

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ABSTRACT. Excess molar volumes, viscosities, excess viscosities and excess molar activation energies of viscous flow are reported for binary mixtures of sulfolane with benzene, toluene, p-xylene and mesitylene. The excess molar volumes, excess viscosities and excess molar activation energies of viscous flow are negative over the whole mole fraction range at 298.15 K.

Sulfolane is a highly dense, highly polar, aprotic solvent with fairly high dipole moment (4.8 D). It has been used in petroleum industry for the recovery of high purity monocyclic aromatic hydrocarbons, particularly benzene, toluene, and xylenes from naphthas and hydrogenated pyrolysis gasolines. The physical and thermodynamic properties of some binary and ternary mixtures containing sulfolane as a common solvent were studied previously (Benoit and Choux 1968, Jannelli *et al.* 1983, 1984, Karvo 1980a, 1980b, Karvo 1983, Lopex *et al.* 1982 and Sacco and Rakshit 1975). The excess volume and viscosity of some binary mixtures of sulfolane with benzene and toluene were reported elsewhere (Jannelli and Sacco 1972, Nissema and Karvo 1979 and Sacco and Jannelli 1972). To obtain a complete picture of the volumetric and viscometric behaviour of sulfolane and aromatic hydrocarbon mixtures, we report the excess molar volumes, viscosities, excess viscosities and excess molar activation energies of viscous flow for sulfolane + benzene, + toluene, + p-xylene and + mesitylene at 298.15 K.

Experimental

Materials

Sulfolane (Fluka AG, purum) were purified as described elsewhere (Karvo 1983). Benzene, toluene, p-xylene and mesitylene (Fluka AG, puriss) were used

without further purifications. All liquids were stored over freshly actiated molecular sieve of type 3A before use. Densities and viscosities of the pure liquids were measured at 298.15 K and listed in Table 1, together with the literature values for comparison (Fujihara *et al.* 1983, Timmermans 1965, Renon *et al.* 1971, Riddick and Bunger 1970, and Al-Madfai *et al.* 1985). Binary mixtures of sulfolane and aromatic hydrocarbons were prepared on a weight basis. The mole fraction error is estimated to be less than 2×10^{-4} .

Table 1. Densities (g cm^{-3}) and viscosities (cP) of the pure component liquids at 298.15 K.

Component	d (g cm^{-3})		ζ (cP)	
	obs.	lit.	obs.	lit.
Benzene	0.87366	0.87363 ^a	0.607	0.599 ^b
Toluene	0.86219	0.86222 ^a	0.554	0.552 ^c
p-Xylene	0.85668	0.85669 ^b	0.615	0.605 ^c
Mesitylene	0.86096	0.86111 ^b	0.667	0.667 ^d
Sulfolane	1.26607	1.27000 ^c	11.605	--

^aFujihara *et al.* 1983, ^bTimmermans 1965, ^cRiddick and ^dBunger 1970, Al-Madfai *et al.* 1985, ^eRenon *et al.* 1971.

Techniques

a) *Densities.*—Densities of the pure liquids and binary mixtures were determined with digital Anton Paar densimeter (DMA 602) with a thermostated bath controlled to ± 0.01 K. The overall precision of the densities measured was estimated to be better than $3 \times 10^{-6} \text{g cm}^{-3}$.

b) The viscosities were determined using a suspended-level Ubbelohde viscometer in a bath controlled to ± 0.01 K at 298.15 K. The temperature was measured by a Hewlett-Packard quartz thermometer. The flow time was determined electronically using an electronic timer (Schott-Gerate model AVS 300) with a precision ± 0.01 sec.

Results and Discussion

The experimental excess volume, V^E results obtained from the precise density measurements of the binary mixtures of an aromatic hydrocarbon and sulfolane were determined from the following equation:

$$V^E (\text{cm}^3 \text{mol}^{-1}) = x_1 M_1 (d_1 - d) / dd_1 + x_2 M_2 (d_2 - d) / dd_2 \quad (1)$$

where d is the density of solution, d_i , M_i and x_i respectively are the density, molecular weight and mole fraction of the aromatics ($i=1$) and sulfolane ($i=2$). The imprecision of the determination of the V^E is estimated to be less than $2 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$. The experimental values of V^E at 298.15 K are given in Table 2 and presented graphically in Fig. 1. Each set of results was fitted to an empirical equation of the form:

$$V^E (\text{cm}^3 \text{mol}^{-1}) = x(1-x) \sum_{j=0}^k A_j (1-2x)^j \quad (2)$$

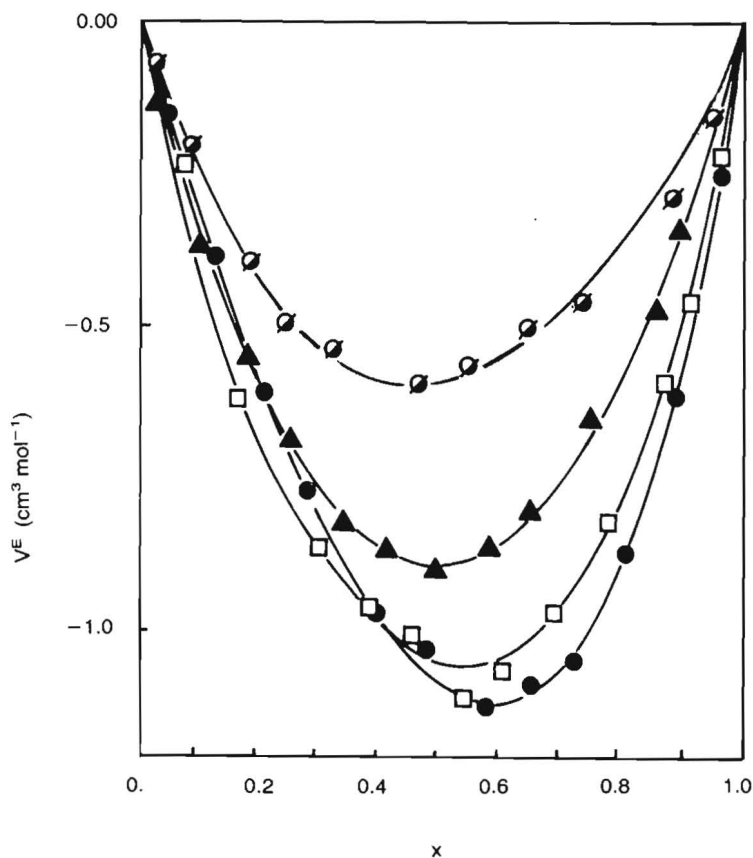


Fig. 1. Excess molar volumes, V^E for x an aromatic hydrocarbon + $(1-x)$ sulfolane at 298.15 K. (●) benzene; (□) toluene; (▲) p-xylene; (◊) mesitylene.

Table 2. Excess molar volumes V^E , viscosities ζ , excess viscosities $\Delta \ln \zeta$, and excess molar Gibbs free energies of activation for viscous flow of ΔG^{*E} of x an aromatic hydrocarbon + $(1-x)$ sulfolane at 298.15 K.

x	$V^E(\text{cm}^3\text{mol}^{-1})$	ζ (cP)	$\Delta \ln \zeta$ (cP)	$\Delta G^{*E}(\text{Jmol}^{-1})$
x Benzene + (1-x) sulfolane				
0.04407	-0.1482	9.816	-0.037	- 97
0.12457	-0.3887	7.357	-0.088	-229
0.21339	-0.6097	5.500	-0.117	-306
0.28474	-0.7636	4.370	-0.136	-358
0.40263	-0.9660	3.053	-0.147	-391
0.48896	-1.0296	2.345	-0.156	-414
0.58355	-1.1220	1.807	-0.138	-372
0.65476	-1.0860	1.482	-0.126	-342
0.73176	-0.0452	1.210	-0.102	-280
0.80924	-0.8694	0.985	-0.078	-217
0.89149	-0.6136	0.799	-0.045	-129
0.97175	-0.2498	0.650	-0.013	- 40
x Toluene + (1-x) sulfolane				
0.07321	-0.2324	8.524	-0.085	-219
0.16821	-0.6175	5.890	-0.167	-428
0.30475	-0.8633	3.637	-0.233	-598
0.38262	-0.9677	2.798	-0.259	-662
0.46600	-1.0084	2.180	-0.255	-654
0.54888	-1.1067	1.712	-0.244	-630
0.61324	-1.0641	1.418	-0.238	-612
0.69652	-1.9678	1.150	-0.193	-499
0.78487	-0.8193	0.915	-0.153	-396
0.87245	-0.5904	0.740	-0.099	-258
0.91497	-0.4590	0.672	-0.066	-173
0.96085	-0.2210	0.604	-0.033	- 88
x p-Xylene + (1-x) sulfolane				
0.02852	-0.1378	10.367	-0.029	- 74
0.10157	-0.3679	7.458	-0.144	-359
0.18214	-0.5489	5.342	-0.241	-598
0.25377	-0.6830	4.099	-0.295	-732
0.34369	-0.8213	3.076	-0.318	-789
0.41799	-0.8647	2.437	-0.333	-825
0.50520	-0.8985	1.921	-0.315	-779
0.58526	-0.8586	1.574	-0.300	-690
0.65395	-0.7987	0.298	-0.270	-667
0.75753	-0.6536	1.026	-0.201	-497
0.85483	-0.4700	0.819	-0.140	-346
0.89867	-0.3374	0.752	-0.097	-240
x Mesitylene + (1-x) sulfolane				
0.02750	-0.0729	10.557	-0.016	- 37
0.08440	-0.2065	8.319	-0.092	-218
0.18331	-0.3984	5.739	-0.181	-428
0.24667	-0.4934	4.649	-0.210	-497
0.38951	-0.6239	3.050	-0.224	-524
0.46573	-0.5922	2.438	-0.230	-537
0.55086	-0.5639	1.935	-0.218	-507
0.64675	-0.5010	1.512	-0.191	-423
0.74137	-0.4579	1.200	-0.152	-352
0.88988	-0.2836	0.834	-0.092	-216
0.95077	-0.1560	0.730	-0.051	-121

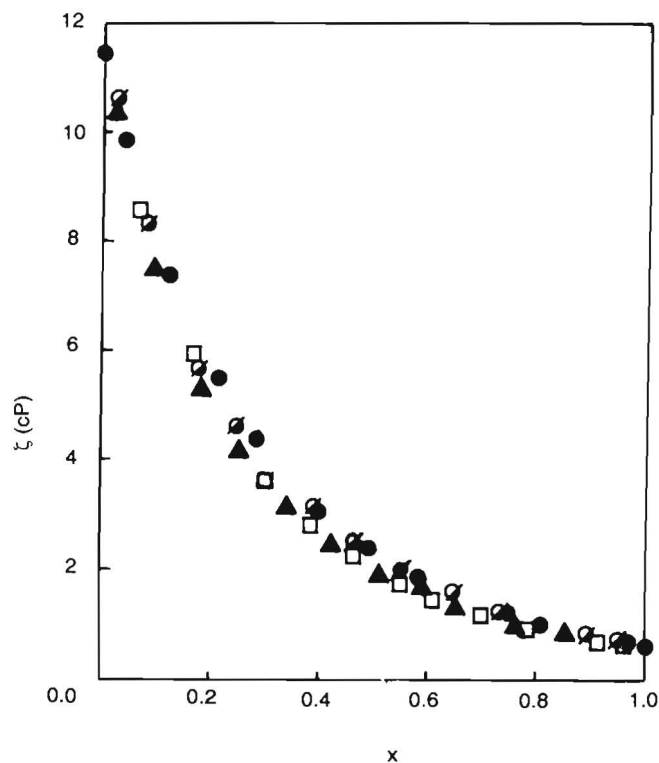


Fig. 2. Viscosities, ζ for x an aromatic hydrocarbon + $(1-x)$ sulfolane at 298.15 K. (●) benzene; (□) toluene; (▲) *p*-xylene; (○) mesitylene.

Table 3. Coefficients A_j and standard deviation SD for least-squares representations of V^E ($\text{cm}^3 \text{mol}^{-1}$) by equation (2).

A_j	Benzene	Toluene	<i>p</i> -Xylene	Mesitylene
A_0	-4.3706	-4.1886	-3.6046	-2.3722
A_1	0.9886	0.2047	0.0896	-0.6154
A_2	0.7236	-1.8038	0.7387	-0.3635
A_3	1.9444	1.4840	-0.4783	1.2004
A_4	-3.2199	1.6108	-2.0821	-0.5418
SD	3.8×10^{-8}	3.8×10^{-8}	3.8×10^{-8}	6.4×10^{-8}

The values of the coefficients A_j are listed in Table 3, together with the standard deviation (SD).

Experimental viscosities (ζ) are listed in Table 2 and plotted in Fig. 2. Excess molar viscosities $\Delta \ln \zeta$ and excess molar activation energies of viscous flow, ΔG^{*E} were calculated from the following equations (Delmas *et al.* 1975 and Heric and Coursey 1972).

$$\Delta \ln \zeta \text{ (cP)} = \ln \zeta - (x \ln \zeta_1 + (1-x) \ln \zeta_2) \quad (3)$$

$$\Delta G^{*E} (\text{J mol}^{-1}) = RT [\ln \zeta V - (x \ln \zeta_1 V_1 + (1-x) \ln \zeta_2 V_2)] \quad (4)$$

where ζ and V are respectively the viscosity and molar volume of the mixture. ζ_i and V_i represent the viscosity and molar volume of the i th component. R and T have their usual meanings. The obtained results of $\Delta \ln \zeta$ and ΔG^{*E} are listed in Table 2 and illustrated in Figs. 3 and 4, respectively over the whole mole fraction range.

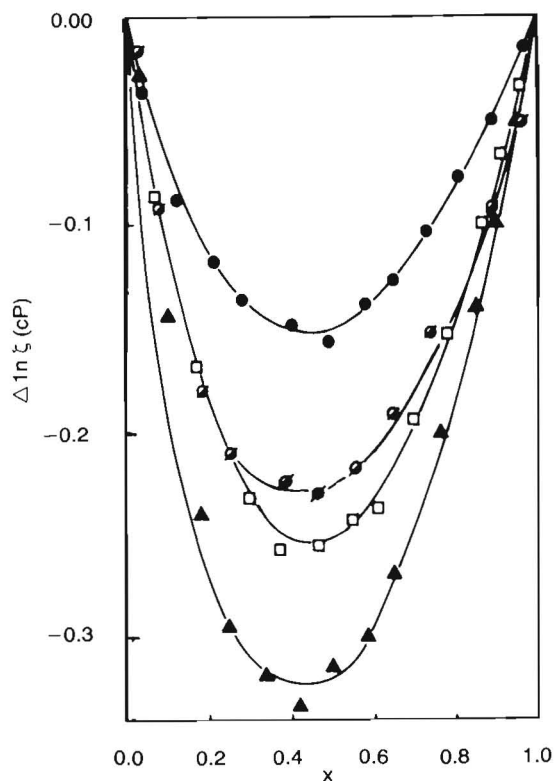


Fig. 3. Excess molar viscosities, $\Delta \ln \zeta$ for x an aromatic hydrocarbon + $(1-x)$ sulfolane at 298.15 K. (●) benzene; (□) toluene; (▲) *p*-xylene; (◊) mesitylene.

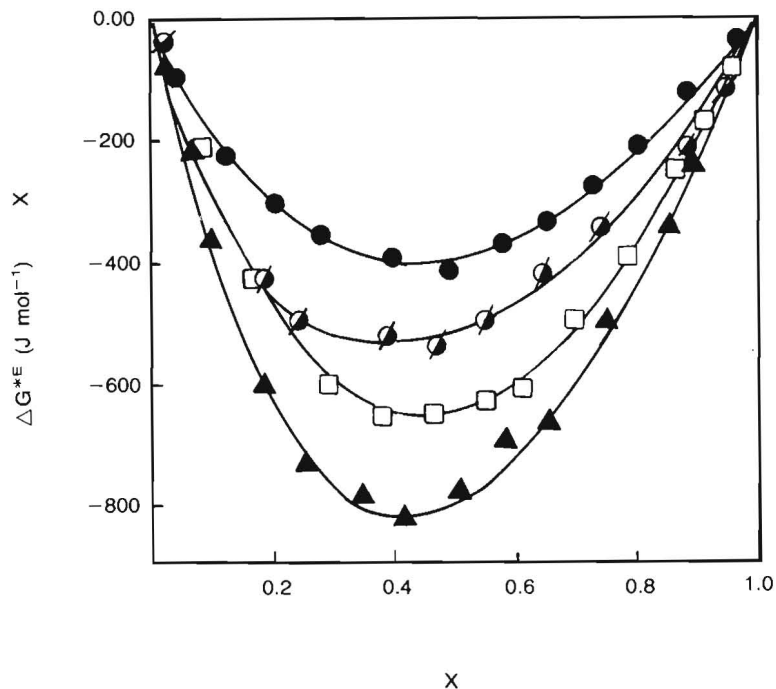


Fig. 4. Excess molar Gibbs free energy of activation of viscous flow, ΔG^{*E} for x an aromatic hydrocarbon + $(1-x)$ sulfolane at 298.15 K. (●) benzene; (□) toluene; (▲) p-xylene; (○) mesitylene.

Volumetric behaviour

The excess molar volumes V^E for all the binary mixtures, Fig. 1, are negative over the whole mole fraction range at 298.15 K. The excess molar volumes obtained here can be explained qualitatively by the dipole - induced dipole interaction between the benzene ring of the aromatic hydrocarbon and the sulfone group of the sulfolane, which is greater than the dispersive and dipole - dipole breaking interactions. Our results of V^E at $x = 0.5$ for benzene system is $1.0926 \text{ cm}^3 \text{ mol}^{-1}$ which agrees very well with those published by Sacco $1.0920 \text{ cm}^3 \text{ mol}^{-1}$ (Sacco and Jannelli 1972). It seems that the excess molar volume decreases as the substitution of the methyl group in the benzene ring increases (Fig. 1). The value of V^E decreases in the sequence: benzene > toluene > p-xylene > mesitylene. This is probably due to the steric effects associated with the methyl substituents.

Viscometric Behaviour

The experimental data of the viscosity are presented in Fig. 2 as a function of the mole fraction x of an aromatic hydrocarbon. All mixtures deviate from ideality and show negative deviation. Excess molar viscosities, $\Delta \ln \zeta$ obtained from

equation 3 are plotted against the mole fraction x of an aromatic hydrocarbon (Fig. 3) are negative for all the mixtures and over the whole mole fraction range at 298.15 K. ΔG^{*E} obtained from equation 4 are plotted in Fig. 4 as a function of the mole fraction x of an aromatic hydrocarbon. ΔG^{*E} is negative over the whole mole fraction range.

Such viscometric behaviour obtained here can be explained by the dipole - induced dipole interaction between the sulfone group in the sulfolane and the benzene ring is greater than the dipole breaking interaction. This hypothesis is substantiated by the negative volume of mixing obtained. Since $\Delta \ln \zeta$ and ΔG^{*E} do not follow the volume of mixing sequence, these may reflect another important factors which have contributions; the inductive, the steric and the geometrical factors. It is apparent that the magnitude of ΔG^{*E} for benzene is smaller than for toluene and p-xylene systems, the minimum value at $x = 0.5$ is (-402 J mol^{-1}) for the benzene system; (-657 J mol^{-1}) for the toluene system; and (-785 J mol^{-1}) for the p-xylene system. Because of the inductive effect of the methyl group in the toluene and p-xylene, the electrostatic interaction and the dispersive force in pure toluene and p-xylene are considered to be weaker than those in pure benzene. Therefore, the degree to which such molecular interactions are lessened as a result of introducing sulfolane molecules may be smaller in the benzene system. This enhance the dipole - induced dipole interaction to give highest negative ΔG^{*E} values are smaller, which may be attributed to the steric hindrance of methyl groups and the geometrical factors, this is supported by the lowest negative V^E obtained.

Conclusions

The excess molar volume V^E for all the binary mixtures studied are negative over the whole mole fraction range and decreases with introducing the methyl group in the benzene ring. The viscosity show a decrease in its value as the concentration of aromatic hydrocarbons increases. The excess viscosity and excess activation energy show a large negative deviation from ideality and follow the same pattern. Such behaviours in these binary mixtures may be due to the dipole - induced dipole interactions between the sulfone group in the sulfolane and the benzene ring, and the steric effects associated with the methyl substituents.

Acknowledgement

The authors are indebted to the Scientific Research Council of Iraq for the support during all the periods of the research.

References

- Al-Madfai, S.F., Awwad, A.M., and Jbara, K. (1985) Some properties of binary mixtures of N-formylmorpholine and an aromatic hydrocarbon, *Thermochimica Acta* **84**: 33-40.
- Benoit, R.L. and Choux, G. (1968) Reactions dans le sulfolane. III. Etude des interactions eau - sulfolane, *Cand. J. Chem.* **46**: 3215-3219.
- Delmas, G., Purves, P. and de st. Romain, P. (1975) Viscosities of mixtures of branched and normal alkanes with tetrabutyltin. Effect of the orientational order of longchain alkanes on the entropy of mixing, *J. Phys. Chem.* **79**: 1970-1975.
- Fujihara, I., Kobayashi, M. and Murakami, S. (1983) Molar excess volumes of trans-declain + benzene, + toluene, + isooctane and + n- heptane at 298.15 K., *Fluid Phase Equilibria* **15**: 81-89.
- Heric, E.L. and Coursey, B.M. (1972) Some properties of binary systems of hexane and normal chloroalkanes, *J. Chem. Eng. Data* **17**: 41-44.
- Jannelli, L., Lopez, A., and Silvestri, L. (1983) Thermodynamic and physical properties of binary mixtures involving sulfolane. 2. Excess dielectric constants of mixing sulfolane and propionitrile, butyronitrile valeronitrile, *J. Chem. Eng. Data* **28**: 166-169.
- Jannelli, L., Pansini, M. and Jالenti, R. (1984) Partial molar volumes of C₂-C₅ normal and branched nitriles in dilute sulfolane solutions at 30°C, *J. Chem. Eng. Data* **29**: 263-266.
- Jannelli, L. and Sacco, A. (1972) Thermodynamic and physical behavior of binary mixtures involving sulfolane. II. Viscosity, dielectric constant, solid + liquid phase diagram of mixtures of benzene + sulfolane, *J. Chem. Thermodyn.* **4**: 715-722.
- Karvo, M. (1980a) Thermodynamic properties of binary and ternary mixtures containing sulfolane. V. Excess enthalpies of cyclohexane + benzene, cyclohexane + toluene, benzene + sulfolane and toluene + sulfolane, *J. Chem. Thermodyn.* **12**: 635-639.
- Karvo, M. (1980b) Thermodynamic properties of binary and ternary mixtures containing sulfolane. VI. Vapour liquid equilibriums for (benzene + sulfolane) and (toluene + sulfolane), *J. Chem. Thermodyn.* **12**: 1175-1181.
- Karvo, M. (1983) Excess enthalpies of sulfolane + benzene, + toluene, + p-xylene, and + mesitylene as functions of temperature, *J. Chem. Thermodyn.* **15**: 821-825.
- Lopez, A., Jannelli, L. and Silvestri, L. (1982) Thermodynamic properties of binary mixtures involving sulfolane. I. Excess volumes on mixing sulfolane and propionitrile, butyronitrile, and valeronitrile, *J. Chem. Eng. Data* **27**: 183-186.
- Nissema, A. and Karvo, M. (1979) Thermodynamic properties of binary mixtures containing sulfolane. Part III. Excess molar volumes of benzene + sulfolane and toluene + sulfolane systems, *Finn. Chem. Lett.* **3**: 65-68.
- Renon, H., Raimbault, C., and Jeanjean, P. (1971) Extraction des hydrocarbones aromatiques par le dimethylsulfoxyde. *8th World Petroleum Congress* **4**: 197-203.
- Riddick, J.A. and Bunger, W.B. (1970) *Techniques of Chemistry, Organic Solvents*, Volume II, Wiley-Intersciences, New York.
- Sacco, A. and Jannelli, L. (1972) Thermodynamic behaviour of binary mixtures involving sulfone. I. Excess volumes of sulfolane with benzene, carbon tetrachloride, and dioxan, *J. Chem. Thermodyn.* **4**: 191-197.

- Sacco, A. and Rakshit, A.K.** (1975) Thermodynamic and physical properties of binary mixtures involving sulfolane. III. Excess volumes of sulfolane with each of nine alcohols, *J. Chem. Thermodyn.* 7: 257-261.
- Timmermans, J.** (1965) *Physico-chemical Constants of Pure Organic Compounds*, Volume II, Elsevier, Amestrdam.

(Received 27/10/1987;
in revised form 23/04/1988)

الحجوم الفائضة واللزوجة في المخاليط الثنائية للهدروكربونات العطرية والسلفولان في درجة ٢٩٨,١٥ مطلقاً

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مركز بحوث النفط - الجادرية - ص. ب. ١٠٠٣٩ - بغداد - العراق

إن الأهمية الصناعية للسلفولان كمذيب قطبي تكمن في كونه ذو كفاءة عالية في انتقاء الهيدروكربونات العطرية إحادية الحلقة (البنزين، التلوين والزايلينات) من المشتقات النفطية. حيث إنه يستخدم على نطاق صناعي كبير في استخلاص الهيدروكربونات العطرية من الريفورميت والكازولين والنافثا الخفيفة. تمت دراسة الخواص الديناميكية والثرموديناميكية لعدة مخاليط تحتوي على هذا المذيب لمعرفة سلوكيته. في هذا البحث، تم تعيين كل من الكثافة واللزوجة لمخاليط مختلفة من البنزين والتلوين والبارازايلين والمستيلين مع السلفولان في درجة ٢٩٨,١٥ مطلقاً. كما تم حساب الحجم الفائضة، اللزوجة الفائضة وطاقة التنشيط الفائضة من الكثافة واللزوجة المقاسة عملياً لتلك المذيبات النقية ومخاليطها. يتضح من النتائج التي تم الحصول عليها أن هناك حيوداً عن المثالية بالإتجاه السالب نتيجة للتداخلات الجزيئية بين مجموعة السلفون في مذيب السلفولان وحلقة البنزين في المركبات الهيدروكربونية العطرية على كل مدى الكسر المولي في درجة ٢٩٨,١٥ مطلقاً.