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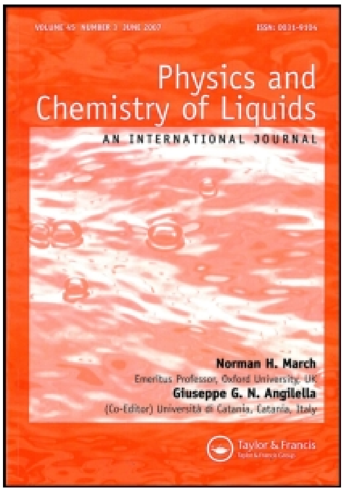

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Densities and Viscosities of the Binary Mixtures Decanol Some *n*-Alkanes at 298.15 K

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DENSITIES AND VISCOSITIES OF THE BINARY MIXTURES DECANOL + SOME *n*-ALKANES AT 298.15 K

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Densities and viscosities of four binary liquid systems decanol +*n*-heptane, +*n*-octane, +*n*-nonane, +*n*-decane, have been determined at 298.15 K and atomospheric pressure, over the complete composition ranges. The excess values of molar volume, viscosity and Gibbs free energy for the activation of flow were evaluated. The Grunberg-Nissan parameter was also calculated. The viscosity data were fitted to the equations of McAllister and Auslander.

KEY WORDS: Excess molar volumes, excess viscosities, activation energies.

INTRODUCTION

The present paper forms a part of our programme on the measurement of transport properties of non-electrolyte solutions containing alcohols as a common component. Densities and viscosities of binary mixtures of decanol +*n*-heptane, +*n*-octane, +*n*-nonane, and +*n*-decane have been found experimentally at 298.15 K and atmospheric pressure in order to analyse the molecular interactions in these systems.

The measured data were used to calculate the excess molar volume, excess viscosity, excess Gibbs free energy for activation of flow and the Grunberg–Nissan parameter.

Different approaches have been suggested to the problem of predicting viscosity of mixtures. In the present work we have selected the semi-empirical relations of McAllister and Auslander.

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EXPERIMENTAL SECTION

All the chemicals used in the present study were supplied by Sigma and were used as received. No further purification treatment was carried out. The stated purity of all the chemicals exceeded 99.0 mol % except for the purity of decanol which was higher than 98.0 mol %.

All the solutions were prepared by using a Mettler H51 balance (precision of 1×10^{-5} g) and air-tight stoppered bottles. The error in the mole fraction is estimated to be lower than 5×10^{-5}.

Densities of the pure components and their mixtures were measured with an Anton Paar Model DMA 60/602 densimeter with a resolution of 1.5×10^{-6} g.cm^{-3}. The density determination is based on measuring the period of oscillation of the vibrating U-shaped sample tube, filled with the sample. Deionized double-distilled water and dry air were chosen as calibrating fluids since their densities are known at a high precision level. Calibration was carried out before each measurements at the same temperature and pressure conditions. The temperature of the thermostat was maintained constant to within ±0.01 K. Temperature was detected with a digital precision thermometer (Anton Paar DT 100-20).

Kinematic viscosities of the pure liquids and mixtures at different concentrations were measured with a Schott-Geräte measuring system, consisting of a measuring stand, an automatic washer, a constant-temperature bath and a calibrated Ubbelohde suspended level viscometer. Time measurements were made automatically using two TC sensors across the viscometer and an electronic timer (Schott AVS 440) with a precision of ±0.01 s. The thermostat bath (CT 1450) was controlled to within ±0.01 K. The Hagenbach correction of the kinematic viscosity was carried out automatically on account of flow time. Consequently the precision of the kinematic viscosity data was estimated to be higher than 5×10^{-4} mm^2/s.

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RESULTS

Table 1 report the results of the measurements in terms of mole fractions for the systems investigated. The table includes density data (ρ) and kinematic viscosity (ν) (quantities directly measured), together with the dynamic viscosities (η), the Grunberg–Nissan parameter (d), the excess volumes (v^E), the excess dynamic viscosities (η^E) and the excess molar Gibbs free energy of activation of flow ($^*G^E$).

Grunberg–Nissan[1] suggested the expression

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \tag{1}$$

where d is a parameter proportional to the interchange energy. The excess molar volumes are calculated with the following equation

$$v^E = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1}) \tag{2}$$

Table 1 Mole Fraction (x_1) of decanol, density (ρ), kinematic viscosity (ν), dynamic viscosity (η), Grunberg–Nissan parameter (d) Excess volume (v^E), excess dynamic viscosity (η^E), and Gibbs Free energy ($*G^E$) for various binary mixtures.

x_1	ρ g/cm^3	ν mm^2/s	η $mPa\ s$	d	v^E cm^3/mol	η^E $mPa\ s$	$*G^E$ J/mol
decanol + *n*-heptane							
0.0000	0.67963	0.594	0.404	—	0.0000	0.000	0.0
0.1049	0.69960	0.816	0.571	−0.08	−0.1180	−1.028	−12.1
0.1860	0.71426	1.049	0.749	−0.06	−0.2122	−1.774	−13.0
0.2545	0.72612	1.295	0.940	−0.07	−0.2871	−2.363	−21.0
0.3641	0.74402	1.824	1.357	−0.07	−0.3663	−3.195	−26.2
0.4174	0.75229	2.158	1.623	−0.07	−0.3907	−3.536	−27.4
0.5198	0.76737	2.993	2.297	−0.06	−0.3992	−4.030	−23.9
0.6066	0.77946	3.957	3.084	−0.06	−0.3883	−4.231	−20.1
0.7074	0.79270	5.467	4.334	−0.07	−0.3426	−4.130	−22.6
0.7806	0.80184	6.931	5.558	−0.07	−0.2947	−3.741	−20.7
0.8420	0.80923	8.472	6.856	−0.07	−0.2485	−3.142	−16.5
0.8975	0.81560	10.165	8.291	−0.07	−0.1787	−2.339	−12.1
0.9561	0.82209	12.332	10.138	−0.08	−0.0929	−1.160	−6.5
1.0000	0.82671	14.271	11.798	—	0.0000	0.000	0.0
decanol + *n*-octane							
0.0000	0.69846	0.763	0.533	—	0.0000	0.000	0.0
0.1016	0.71354	0.986	0.704	−0.41	−0.0200	−0.974	−89.2
0.1773	0.72457	1.210	0.877	−0.35	−0.0632	−1.654	−123.8
0.2609	0.73644	1.510	1.112	−0.38	−0.1109	−2.360	−175.6
0.3417	0.74758	1.896	1.417	−0.36	−0.1491	−2.965	−194.0
0.4222	0.75838	2.380	1.805	−0.36	−0.1830	−3.484	−212.8
0.4925	0.76755	2.924	2.244	−0.35	−0.2032	−3.837	−212.6
0.5889	0.77973	3.892	3.035	−0.35	−0.2142	−4.132	−205.2
0.6804	0.79089	5.151	4.074	−0.34	−0.2086	−4.124	−178.4
0.7552	0.79972	6.500	5.198	−0.33	−0.1895	−3.842	−149.3
0.8193	0.80707	7.949	6.415	−0.33	−0.1597	−3.347	−120.6
0.8948	0.81551	10.125	8.257	−0.33	−0.1166	−2.356	−75.7
0.9261	0.81892	11.201	9.173	−0.33	−0.0911	−1.793	−55.7
0.9551	0.82201	12.320	10.127	−0.32	−0.0581	−1.165	−33.3
1.0000	0.82671	14.271	11.798	—	0.0000	0.000	0.0
decanol + *n*-nonane							
0.0000	0.71369	0.961	0.686	—	0.0000	0.000	0.0
0.0904	0.72444	1.170	0.848	−0.56	0.0178	−0.843	−112.5
0.1635	0.73312	1.394	1.022	−0.49	0.0121	−1.481	−164.0
0.2509	0.74344	1.722	1.280	−0.48	−0.0065	−2.194	−221.9
0.3373	0.75358	2.150	1.620	−0.45	−0.0370	−2.814	−247.6
0.3984	0.76066	2.151	1.913	−0.45	−0.0525	−3.200	−266.7
0.4735	0.76928	3.065	2.358	−0.45	−0.0693	−3.590	−278.3
0.5541	0.77841	3.790	2.950	−0.48	−0.0798	−3.893	−291.3
0.6142	0.78516	4.472	3.511	−0.48	−0.0880	−4.000	−283.7
0.6776	0.79220	5.323	4.217	−0.51	−0.0904	−3.999	−276.9
0.7461	0.79971	6.489	5.189	−0.52	−0.0850	−3.787	−245.7
0.8529	0.81125	9.003	7.304	−0.49	−0.0671	−2.860	−151.7
0.9452	0.82102	12.029	9.876	−0.42	−0.0332	−1.313	−54.5
1.0000	0.82671	14.271	11.798	—	0.0000	0.000	0.0

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Table 1 (*continuation*)

x_1	ρ g/cm^3	v mm^2/s	η $mPa\ s$	d	v^E cm^3/mol	η^E $mPa\ s$	$*G^E$ J/mol
			decanol + *n*-decane				
0.0000	0.72606	1.183	0.859	—	0.0000	0.000	0.0
0.0771	0.73345	1.380	1.012	−0.53	0.0547	−0.690	−93.1
0.1568	0.74125	1.592	1.180	−0.70	0.0750	−1.394	−229.9
0.2159	0.74712	1.818	1.358	−0.63	0.0722	−1.862	−265.1
0.3219	0.75775	2.262	1.714	−0.70	0.0514	−2.666	−377.1
0.4054	0.76621	2.730	2.092	−0.71	0.0229	−3.202	−426.1
0.4784	0.77362	3.254	2.517	−0.71	0.0018	−3.575	−441.4
0.6063	0.78663	4.513	3.550	−0.71	−0.0261	−3.941	−420.3
0.7002	0.79617	5.950	4.737	−0.61	−0.0312	−3.781	−315.1
0.7774	0.80402	7.355	5.914	−0.62	−0.0293	−3.449	−266.7
0.8602	0.81244	9.400	7.637	−0.57	−0.0200	−2.632	−170.4
0.9529	0.82189	12.399	10.191	−0.51	−0.0063	−1.092	−57.2
1.0000	0.82671	14.271	11.798	—	0.0000	0.000	0.0

excess viscosities by

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

and the excess activation energies, $*G^E$, are calculated by the relation of Reed and Taylor[2]

$$\ln \eta v = x_1 \ln \eta_1 v_1 + x_2 \ln \eta_2 v_2 + {*G^E}/RT \tag{4}$$

where x_j is the mole fraction of component j, and for the other parameters (densities ρ, dynamic viscosities η, molar volumes v and molecular weight M) the subscript indicated the values corresponding to the pure components and the lack of subscript the values corresponding to mixtures.

Each set of results were fitted with a Redlich–Kister[3] equation of the type

$$X^E = x_1 x_2 \sum_{j=1}^{n} A_j (x_1 - x_2)^{j-1} \tag{5}$$

where A_j are the parameters obtained by a linear least squares fitting procedure. In each case, the optimum number, n, of coefficients was determined using an F-test[4]. The values of parameters A_j and the standard deviations s are summarized in Table 2.

The following predictive equations of solutions viscosities have been tested with the experimental data. McAllister[5] equation derived on the basis of the absolute reaction rate theory of Eyring[6]:

$$\begin{aligned} \ln \eta = {} & x_1^3 \ln \eta_1 + x_2^3 \ln \eta_2 + 3x_1^2 x_2 \ln \eta_{12} + 3x_1 x_2^2 \ln \eta_{21} \\ & - \ln[x_1 + x_2 M_2/M_1] + 3x_1^2 x_2 \ln [2/3 + M_2/3M_1] \\ & + 3x_1 x_2^2 \ln[1/3 + 2M_2/3M_1] + x_2^3 \ln[M_2/M_1] \end{aligned} \tag{6}$$

where η_{12} and η_{21} are the interaction parameters.

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Table 2 Coefficients for Eq. (5) and standard deviation s determined by the method of least squares.

System		A_1	A_2	A_3	A_4	s
decanol + *n*-heptane	v^E	-1.6055	-0.0015	0.0009	-0.7141	0.003
	η^E	-15.798	-8.239	-3.714	-1.447	0.004
	$^*G^E$	-100	-4	-39		3
decanol + *n*-octane	v^E	-0.8160	-0.3689	0.1225	-0.4036	0.002
	η^E	-15.460	-8.186	-3.786	-1.475	0.005
	$^*G^E$	-852	72	-8		4
decanol + *n*-nonane	v^E	-0.2958	-0.3489	0.1739	-0.2298	0.002
	η^E	-14.850	-8.202	-3.839	-0.693	0.011
	$^*G^E$	-1152	-276	-196	602	5
decanol + *n*-decane	v^E	-0.0165	-0.5301	0.4582		0.001
	η^E	-14.650	-7.894	-2.719		0.021
	$^*G^E$	-1757	131	559		14

The Auslander[7] equation, the less complex three-parameter equation, has the following form:

$$x_1(x_1 + B_{12}x_2)(\eta - \eta_1) + A_{21}x_2(B_{21}x_1 + x_2)(\eta - \eta_2) = 0 \tag{7}$$

here A_{21}, B_{12} and B_{21} are the parameters representing binary interactions.

The constants of equations 6 and 7 were determined by the least squares method. Table 3 lists the parameters for these models along with their respective standard deviations.

DISCUSSION

Volumetric behaviour

In Figure 1 we show the behaviour of the excess molar volumes for the mixtures under study. These results show that v^E changes from negative to sigmoid, and the sign of v^E is changed at higher molar fractions of alcohol as the number of carbons in the hydrocarbon increases. When the component molecules are of approximately

Table 3 Computer analysis of parameters of Eq. (6) and (7) and standard deviations s.

System	*McAllister formula*			*Auslander formula*			
	η_{12}	η_{21}	s	A_{21}	B_{12}	B_{21}	s
decanol + *n*-heptane	3.7748	1.2346	0.004	5.0892	0.5676	0.7006	0.003
decanol + *n*-octane	3.7934	1.3264	0.003	5.4034	0.6691	0.6608	0.004
decanol + *n*-nonane	3.8689	1.5304	0.019	7.2616	1.1216	0.4746	0.013
decanol + *n*-decane	4.0089	1.6149	0.036	6.5643	0.9689	0.5034	0.021

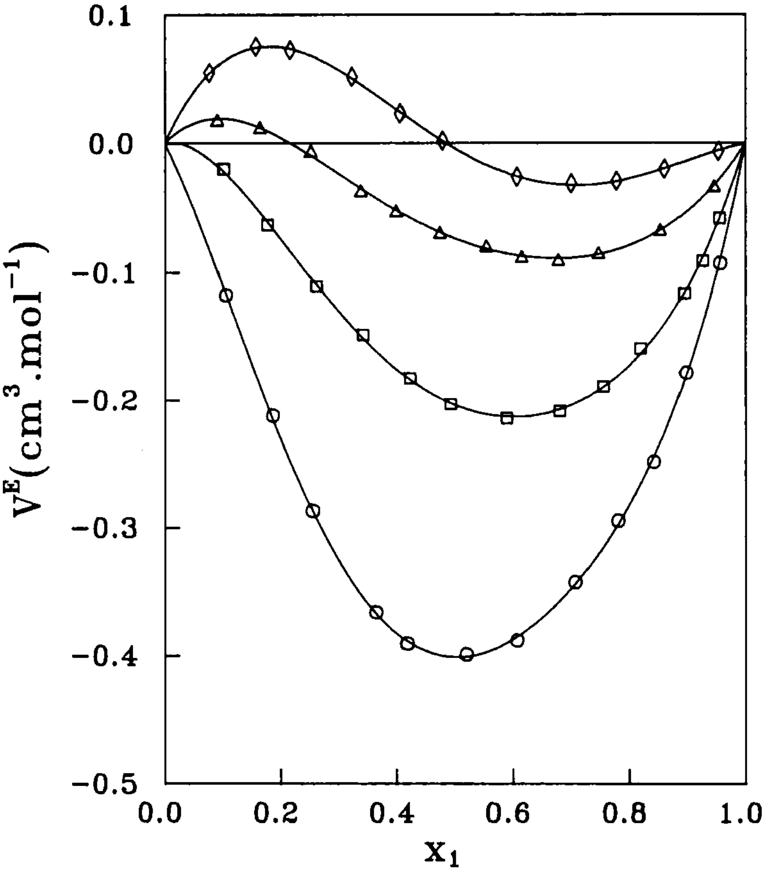

Figure 1 Excess molar volumes at 298.15 K for decanol + n-heptane (○), + n-octane (□), + n-nonane (△), + n-decane (◇). Continuous curves were calculated from Eq. (5).

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equal size, the positive and negative lobes of the curve are approximately equal. This behaviour is similar to that found for cycloalkanol + cycloalkane[8] mixtures. The positive regions of v^E decrease markedly as the length of the n-alkane molecule decreases, which is opposite to what happens in the n-alkane + n-alkanols[9].

In a qualitative way, we can postulate that the values of v^E are the result of opposite effects. The autoassociation of the alcohol produces an increase in this volume, whereas the negative contributions are due to changes in the free volume of the real mixture (which contains monomers and multimers of alcohol and alkane molecules). The latter effect is the cause of the variations observed in the series we study in this work, as the rotating motion of the n-alkane molecules when accommodating in the interstices of the branched stucture of the n-alcohol[8,10] multimers is restricted. Thus, when the length of the n-alkane chain increases, the negative effect accompanying the accommodation of the n-alkane molecules in the structure of n-alcohol multimers decreases in its importance.

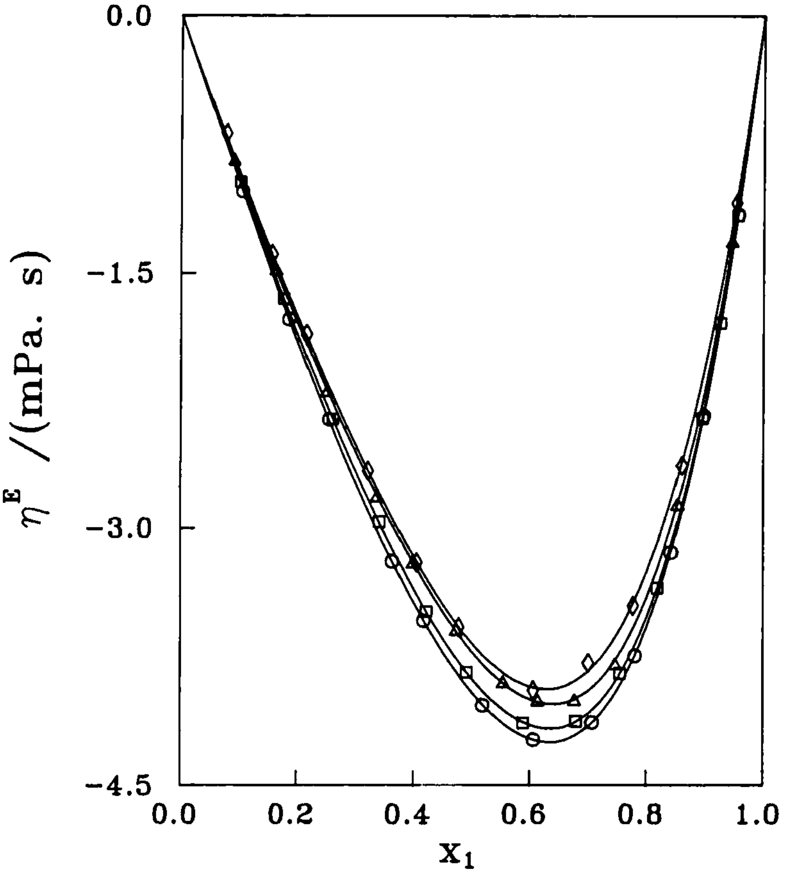

Figure 2 Excess viscosities at 298.15 K for decanol +*n*-heptane (○), +*n*-octane (□), +*n*-nonane (△), +*n*-decane (◇). Continuous curves were calculated from Eq. (5).

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Viscometric behaviour

The results shown in Figure 2 indicate that for all the systems η^E is negative in the whole range of molar fractions, becoming less negative as the length of the hydrocarbon chain increases. The shapes of the visocosity versus the composition curves are characteristic of the systems formed by a substance which presents molecular association and another which does not[11]. Viscosity decreases to a greater extent on the initial addition of hydrocarbon to *n*-decanol. This behaviour is also characteristic of systems in which at least one of the components exhibits intramolecular hydrogen bonding[12], and it is known that intermolecular hydrogen bonding exist in *n*-decanol.

In Figure 3 we show the values of the parameter $^*G^E$ versus the composition for our systems. According to several researchers[13,14], this parameter can be considered as a valid measure for detecting the presence of interactions among the molecules.

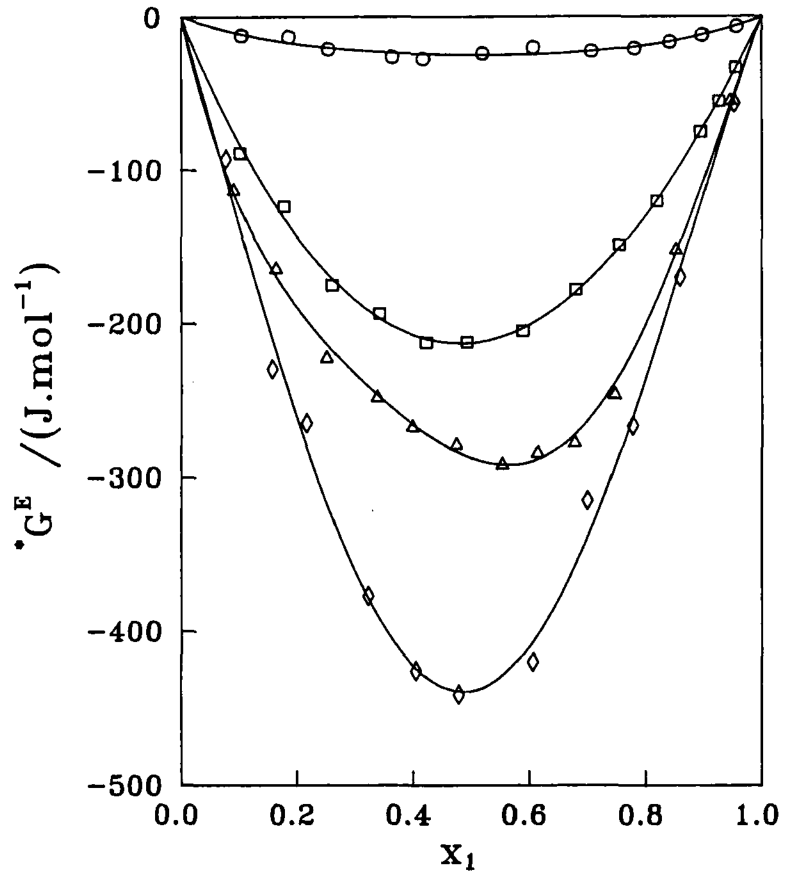

Figure 3 Excess energies for activation for viscous flow at 298.15 K for decanol + *n*-heptane (○), + *n*-octane (□), + *n*-nonane (△), + *n*-decane (◇). Continuous curves were calculated from Eq. (5).

For our systems, the negative values of $^*G^E$ permit us to conclude that only dominant forces are the repulsive ones.

Irving[15] has rigorously analyzed the suitability of different equations proposed for the viscosity of liquid mixtures and found the Grunberg–Nissan equation to have the highest goodness factor for polar-non polar liquid mixtures. Grunberg–Nissan's *d* parameter is negative for systems in which the dispersive forces are predominant and weak[16,17].

Finally, we want to point out that McAllister and Auslander's semiempiric relations produce satisfactory results for the systems studied, and specially good results for the *n*-decanol + *n*-heptane and *n*-decanol + *n*-octane systems.

Acknowledgments

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References

1. L. Grunberg and A. H. Nissan, *Nature (London)*, **164**, 799 (1949).
2. T. M. Reed and T. E. Taylor, *J. Phys. Chem.*, **63**, 58 (1959).
3. O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, **40**, 341 (1948).
4. P. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
5. R. L. McAllister, *AIChE J.*, **6**, 427 (1960).
6. H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).
7. G. Auslander, *Br. Chem. Eng.*, **9**, 610 (1964).
8. G. C. Benson and O. J. Kiyohara, *J. Chem. Eng. Data*, **21**, 362 (1976).
9. A. J. Treszczanowicz and G. C. Benson, *J. Chem. Thermodyn.*, **10**, 967 (1978).
10. G. C. Paraskevopoulos and R. W. Missen, *Trans. Faraday Soc.*, **58**, 869 (1962).
11. M. Liler and D. Kosanovic, *Hidrogen Bonding* (Pergamon Press, London, 1959).
12. G. P. Johari, *J. Chem. Eng. Data*, **13**, 541 (1968).
13. T. M. Reed and T. E. Taylor, *J. Phys. Chem.*, **63**, 58 (1959).
14. R. Meyer, M. Meyer, J. Metzer and A. Peneloux, *J. Chem. Phys.*, **62**, 405 (1971).
15. J. B. Irving, *NEL Report* no. 631 (1977).
16. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, **62**, 1112 (1966).
17. K. Ramamoorthy, *J. Pure Appl. Phys.*, **11**, 554, 556 (1973).

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