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Infinite Dilution Activity Coefficients for Aromatic and Nonaromatic Compounds in *N*-Methylpyrrolidone, Ethylene Glycol, and Mixtures of the Two Solvents

Palmira O. Ferreira, João C. Bastos, and Augusto G. Medina*

Centro de Engenharia Química, Faculdade de Engenharia, Rua dos Bragas, 4099 Porto Codex, Portugal

Mixtures of *N*-methylpyrrolidone (NMP) and ethylene glycol (EG) are used for the industrial recovery of pure aromatic hydrocarbons from petroleum fractions (Arosolvan process). In this paper experimental values of activity coefficients for *n*-hexane, *n*-heptane, benzene, and toluene in NMP and in different mixtures of NMP and EG (mole fraction of EG: 0.220, 0.406, 0.495, 0.615, 0.827) are reported. Measurements of infinite dilution activity coefficients were carried out at three temperatures (37, 45, 55 °C) using the retention time method. UNIFAC interaction parameters between the group NMP and the main groups CH_2, ACH, and $ACCH_2$ were estimated, using the new experimental information and values of activity coefficients at infinite dilution for aromatic and nonaromatic hydrocarbons in the solvent NMP available in the open literature. Experimental results obtained for the mixtures NMP/EG were compared with predictions based on the UNIFAC model.

Introduction

The design and simulation of separation processes requires an accurate knowledge of phase equilibrium conditions of complex multicomponent mixtures which are often impossible to obtain experimentally.

Different authors report the possibility of predicting equilibrium conditions for multicomponent mixtures from binary data using thermodynamic models (*1-5*). In this context activity coefficients at infinite dilution play an important role (*6*). Moreover this information is very useful when selecting the more suitable solvent for any extraction or extractive distillation process.

The open literature refers to several methods for the prediction of activity coefficients at infinite dilution (*7-14*).

Group contribution models such as UNIFAC (*15*, *16*) and ASOG (*17*) are also useful for infinite dilution activity coefficients estimation.

A compilation of the experimental methods available for the direct determination of activity coefficients at infinite dilution was presented by Kikic et al. (*18*). Ebulliometry and gas-liquid chromatography are the experimental techniques more widely used (*19*, *20*). Three different alternatives based on gas-liquid chromatography are available, but the retention time method is the one more often used (*19*, *20*). In this approach the evaluation of activity coefficients at infinite dilution is made by measuring the retention times of the solute in a gas chromatographic column in which the stationary phase is the solvent. The static method (*21*, *22*) is based on the evaluation of the vapor-phase composition in equilibrium with a liquid mixture of known composition at constant temperature. A third method, due to Leroi et al. (*23*), requires the determination of the decrease of the concentration of the solute with time in an inert gas that strips the solute from a very dilute solution.

The present study was carried out as part of a project aiming at the prediction of the equilibrium conditions of the multicomponent mixtures involved in the Arosolvan process (*24*). Liquid-liquid equilibrium data were previously determined for the system *n*-heptane-toluene-NMP/EG (*25*) and *n*-hexane-benzene-NMP/EG (*26*).

In the present paper experimental results for infinite dilution activity coefficients of *n*-hexane, *n*-heptane, benzene, and toluene in NMP and in five NMP/EG mixtures at 37, 45, and 55 °C, determined by the retention time method, are reported. High liquid loadings were used in order to avoid significant adsorption at the gas-liquid interface which may occur for these systems (*27*, *28*).

According to Pecsar and Martin (*29*) the activity coefficient at infinite dilution of a solute (component 2) in a solvent (component 1) is given by eq 1.

$$\ln \gamma_2^\infty = \ln\left(\frac{273.15R}{P_2^0 M_1 V_g^0}\right) - \left(\frac{B_{22} - v_2^0}{RT_{\text{exptl}}}\right)P_2^0 \qquad (1)$$

The relationship which correlates the specific retention volume V_g^0 with gas chromatographic quantities is (*30*)

$$V_g^0 = J\,\frac{F}{W_s}\,\frac{P_0 - P_{H_2O}}{760}\,\frac{273.15}{T_f}(t_r - t_a) \qquad (2)$$

where J is the James-Martin factor (31) defined as

$$J = \frac{3}{2}\,\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \qquad (3)$$

The second virial coefficient, B_{22}, may be calculated by the method of Hayden and O'Connell (*32*).

Current equipment of gas-liquid chromatography can be used for the experimental determination of activity coefficients at infinite dilution by the retention time method. However, some modifications are necessary in order to measure experimental variables such as pressure at the column inlet, temperature, and flow of carrier gas with the required accuracy.

Experimental Section

The components used as solutes (*n*-hexane, *n*-heptane, benzene, and toluene) were used as supplied by Merck. *N*-Methylpyrrolidone (BDH) and ethylene glycol (Carlo Erba) were distilled under vacuum (2 cmHg).

Chromatographic tests, for all the components, showed purities greater than 99.5%. The water content in the purified solvents did not exceed 500 ppm.

The activity coefficients were determined by using Teflon columns, 40 cm and 100 cm long (internal diameter 4 mm), filled with Chromosorb WAW DMCS 80/100 impregnated with 25-30% by weight of each mixture NMP/EG studied. NMP/EG mixtures were dissolved in acetone or diethyl ether and deposited on the support by slow evaporation of the volatile diluents. Columns were then packed and conditioned at ambient temperature for 24 h by using helium at reduced flow rate. The amount of stationary phase in each column was determined by weight difference. Using a gas-liquid chromatograph (Perkin-Elmer, Model Sigma 3) equipped with a thermal conductivity detector and connected to a data station (Perkin-Elmer, Model Sigma 10B) retention times were evaluated at three temperatures (37, 45, 55 °C) injecting 0.2 μL of each solute. These

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Table I. Activity Coefficients at Infinite Dilution (γ^∞) of *n*-Hexane, *n*-Heptane, Benzene, and Toluene in Mixtures of NMP/EG

mole fracn of EG	temp, °C	γ^∞ *n*-hexane	γ^∞ *n*-heptane	γ^∞ benzene	γ^∞ toluene
0 (NMP)	37	14.3	17.6	1.22	1.63
	45	13.9	16.8	1.20	1.49
	55	11.0	13.1	1.10	1.40
0.220	37	21.4	27.9	1.52	2.13
	45	21.7	28.0	1.66	2.34
	55	22.3	28.4	1.85	2.64
0.406	37	39.0	51.1	2.51	3.57
	45	36.9	47.1	2.55	3.62
	55	34.4	43.2	2.63	3.71
0.495	37	53.2	68.9	3.14	4.53
	45	47.6	61.1	3.10	4.44
	55	41.7	53.2	3.07	4.37
0.615	37	77.2	107	4.54	6.82
	45	65.4	88.9	4.20	6.25
	55	53.7	71.6	3.86	5.67
0.827	37	127	191	7.27	11.7
	45	111	160	6.83	10.9
	55	94.4	131	6.40	9.99

temperatures were measured within an accuracy of 0.1 °C by means of a calibrated thermistor. The oven temperature was found to be constant within ±0.2 °C. Higher temperatures could not be considered because significant losses of solvent would occur. In any case a glass presaturator for the carrier gas was used. The actual mass of solvent was determined by weighing the column immediately before and after each run; a linear loss of solvent with time was assumed (*33*). The flow rate of the carrier gas, helium, was kept constant (25-40 cm^3 min^{-1}).

The pressure of the carrier gas at the column inlet was measured by means of a mercury manometer connected to the column.

Dispersion of experimental results was lower than 4% even at 55 °C.

Results and Discussion

Table I summarizes the experimental results at 37, 45, and 55 °C for the infinite dilution activity coefficients of *n*-hexane, *n*-heptane, benzene, and toluene in NMP and in five mixtures NMP/EG (mole fraction of EG: 0.220, 0.406, 0.495, 0.615, 0.827).

Due to the number of experimental values of infinite dilution activity coefficients available for nonaromatic and aromatic hydrocarbons in *N*-methylpyrrolidone it was decided to estimate new UNIFAC interaction parameters based on this information (Table II).

A computer program described in ref *43* was used for the calculations. The same computer program allowed the back calculation of activity coefficients. The new UNIFAC interaction parameters, a_{mn}, are presented in Table III.

In Tables IV and V, which refer to nonaromatic and aromatic hydrocarbons, respectively, experimental and predicted values, using the UNIFAC parameters estimated are compared. A similar comparison is made in Figures 1 and 2 for the hydrocarbons considered in this work (*n*-hexane, *n*-heptane, benzene, toluene). The differences between experimental and calculated results were quantified in terms of the deviation *D*, defined by eq 4, and mean values of 19.6 and 14.1% were obtained for nonaromatic and aromatic hydrocarbons, respectively.

$$D = \frac{|\gamma^\infty_{\text{exptl}} - \gamma^\infty_{\text{calcd}}|}{\gamma^\infty_{\text{exptl}}} \times 100 \qquad (4)$$

The new set of parameters estimated in this study was used to predict the equilibrium conditions of the systems considered by Ferreira et al. (*44*). The differences between experimental and calculated results were quantified in terms of a residual function (*F*) defined by eq 5.

$$F = 100[\sum_k (\text{min}) \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2/6M]^{1/2} \qquad (5)$$

Residual values are presented in Table VI. The mean absolute deviation is 7.1. UNIFAC parameters based on liquid-liquid equilibrium data given in ref *44* led to a mean deviation of 1.9%.

Figures 3 and 4 compare, for one of the systems considered, the experimental binodal and distribution curves with predictions

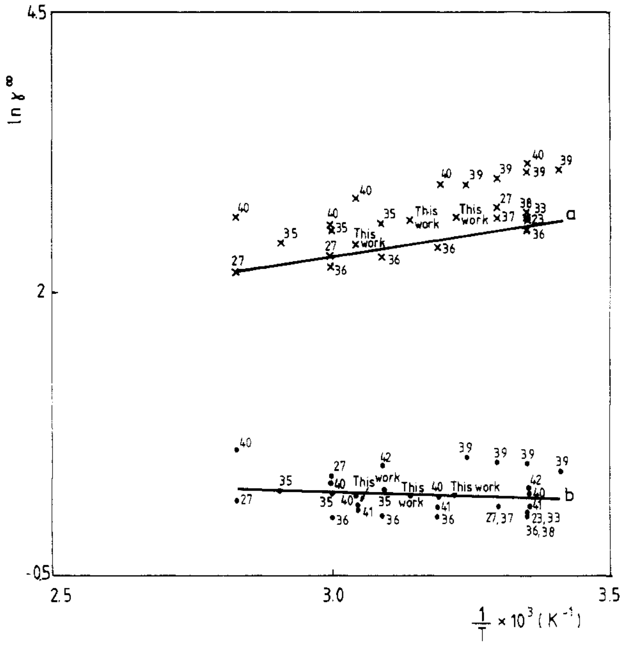

Figure 1. Activity coefficients at infinite dilution of *n*-hexane and benzene in NMP: ×, *n*-hexane; ●, benzene; a, predicted for *n*-hexane by UNIFAC model using the parameters estimated in this work; b, predicted for benzene by UNIFAC model using the parameters estimated in this work.

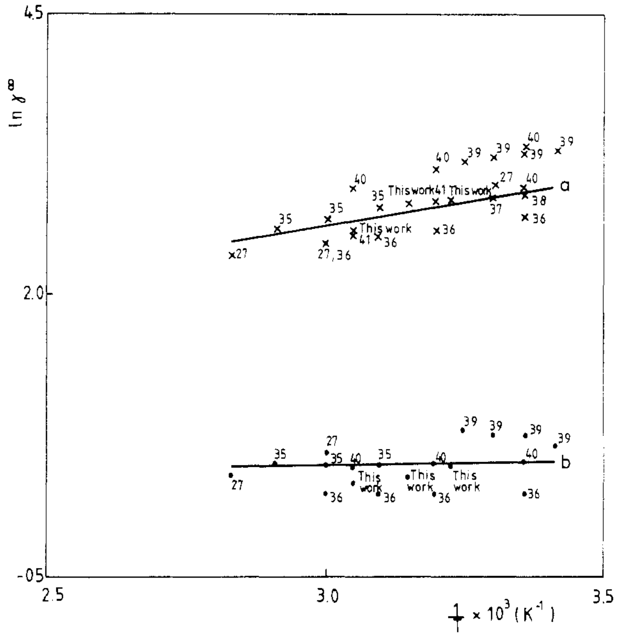

Figure 2. Activity coefficients at infinite dilution of *n*-heptane and toluene in NMP: ×, *n*-heptane; ●, toluene; a, predicted for *n*-heptane by UNIFAC model using the parameters estimated in this work; b, predicted for toluene by UNIFAC model using the parameters estimated in this work.

Table II. References of Data on Infinite Dilution Activity Coefficients of Hydrocarbons in the Solvent NMP Used for Estimation of New UNIFAC Parameters

solute	ref	temp, °C
n-pentane	*27*	30, 60, 80
	34	24, 40
	35	50.2, 60, 70.2
n-hexane	*23*	25
	27	30, 60, 80
	33	25
	35	50.2, 60, 70.2
	36	25, 40, 50, 60
	37	30
	38	25
	39	20, 25, 30, 35
	40	25, 40, 55, 60, 80
	this work	37, 45, 55
n-heptane	*27*	30, 60, 80
	35	50.2, 60, 70.2
	36	25, 40, 50, 60
	37	30
	38	25
	39	20, 25, 30, 35
	40	25, 40, 55
	41	25, 40, 55
	this work	37, 45, 55
n-octane	*27*	30, 60, 80
	35	50.2, 60, 70.2
	36	25, 40, 50, 60
	37	30
	39	20, 25, 30, 35
n-nonane	27	30, 60, 80
	39	20, 25, 30, 35
n-decane	*27*	60, 80
2-methylbutane	*34*	24, 40
2,2,4-trimethylpentane	*35*	50.2, 60, 70.2
cyclopentane	*35*	50.2, 60, 70.2
methylcyclopentane	*35*	50.2, 60, 70.2
	36	25, 40, 50, 60
cyclohexane	*27*	30, 60, 80
	33	25
	35	50.2, 60, 70.2
	36	25, 40, 50, 60
	37	30
	38	25
	39	20, 25, 30, 35
methylcyclohexane	*27*	30, 60, 80
	35	50.2, 60, 70.2
	36	25, 40, 50, 60
	37	30
ethylcyclohexane	*27*	30, 60, 80
	37	30
n-propylcyclohexane	*27*	30, 60, 80
n-butylcyclohexane	*27*	30, 80
benzene	*23*	25
	27	30, 60, 80
	33	25
	35	50.2, 60, 70.2
	36	25, 40, 50, 60
	37	30
	38	25
	39	20, 25, 30, 35
	40	25, 40, 55, 60
	41	25, 40, 55
	42	25, 50
	this work	37, 45, 55
toluene	*27*	60, 80
	35	50.2, 60, 70.2
	36	25, 40, 50, 60
	39	20, 25, 30, 35
	40	25, 40, 55
	this work	37, 45, 55
ethylbenzene	*27*	80

Table III. New UNIFAC Interaction Parameters, a_{mn}[a]

$a_{CH_2,NMP}$	a_{NMP,CH_2}	$a_{ACH,NMP}$	$a_{NMP,ACH}$	$a_{ACCH_2,NMP}$	$a_{NMP,ACCH_2}$
0.4012	196.6436	359.8048	−188.4209	0.0631	69.3262

[a] $a_{mn} = (u_{mn} - u_{nn})/R$ (K).

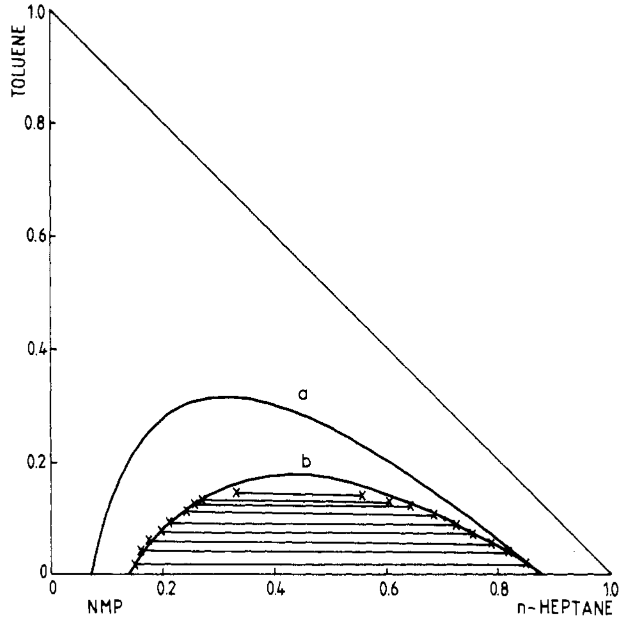

Figure 3. Experimental tie lines and binodal curves predicted by UNIFAC model for NMP (1) + toluene (2) + *n*-heptane (3) at 25 °C (concentrations expressed as mole fractions): ×, experimental points; a, parameters estimated in this work; b, parameters estimated by Ferreira et al. (*44*).

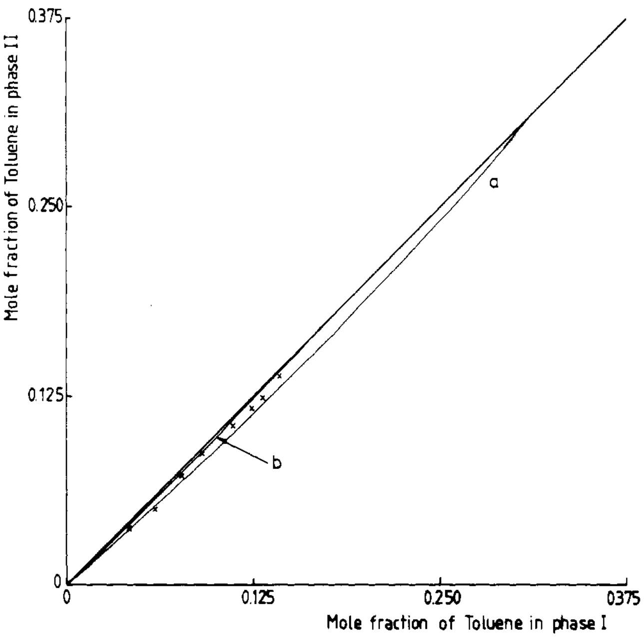

Figure 4. Distribution curves for NMP (1) + toluene (2) + *n*-heptane (3) at 25 °C (concentrations expressed as mole fractions): ×, experimental points; a, parameters estimated in this work; b, parameters estimated by Ferreira et al. (*44*).

based on the two sets of parameters.

For the mixtures NMP/EG studied a comparison between experimental values of γ^∞ and predictions by the UNIFAC model was carried out. A set of interaction parameters based on vapor–liquid equilibrium data (VLE) (*45*) and on values of activity coefficients at infinite dilution (γ^∞) (present work) was used.

Interaction parameters between the groups NMP and DOH (1,2-ethanediol = ethylene glycol)—$a_{NMP,DOH}$ = −283.00; $a_{DOH,NMP}$ = 493.75—were estimated from liquid–liquid equilibrium data available for the system *N*-methylpyrrolidone–benz-

Table IV. Comparison between Experimental Results and Predicted Values for Nonaromatic Hydrocarbons in NMP Using the UNIFAC Model

solute	temp, °C	ref	$\gamma^\infty_{\mathrm{exptl}}$	$\gamma^\infty_{\mathrm{calcd}}$	mean dev
n-pentane	24	31	13.8	9.44	
	40	31	10.2	8.43	
	50.2	32	11.5	7.90	
	60	32	10.2	7.44	22.3
	70.2	32	9.35	7.02	
	30	33	12.3	9.04	
	60	33	8.26	7.44	
	80	33	7.40	6.66	
n-hexane	25	23	13.6	13.2	
	25	30	14.3	13.2	
	50.2	32	13.5	10.9	
	60	32	12.7	10.1	
	70.2	32	11.6	9.47	
	30	33	15.6	12.7	
	60	33	9.91	10.1	
	80	33	8.83	8.91	
	25	34	12.9	13.2	
	40	34	10.8	11.7	
	50	34	10.0	10.9	
	60	34	9.20	10.1	
	30	35	14.2	12.7	19.7
	25	36	14.8	13.2	
	20	37	21.8	13.8	
	25	37	21.0	13.2	
	30	37	20.3	12.7	
	35	37	18.9	12.2	
	25	39	23.0	13.2	
	40	39	20.0	11.7	
	55	39	17.0	10.5	
	60	39	13.4	10.1	
	80	39	14.3	8.91	
	37	this work	14.3	12.0	
	45	this work	13.9	11.3	
	55	this work	11.0	10.5	
n-heptane	50.2	32	16.3	14.8	
	60	32	14.7	13.7	
	70.2	32	13.4	12.7	
	30	33	19.9	17.7	
	60	33	11.8	13.7	
	80	33	10.5	11.8	
	25	34	15.1	18.6	
	40	34	13.1	16.2	
	50	34	12.3	14.8	
	60	34	11.5	13.7	
	30	35	17.7	17.7	
	25	36	18.5	18.6	
	20	37	27.1	19.5	15.9
	25	37	26.7	18.6	
	30	37	25.3	17.7	
	35	37	24.3	16.9	
	25	38	19.1	18.6	
	40	38	17.2	16.2	
	55	38	12.6	14.2	
	25	39	28.0	18.6	
	40	39	23.0	16.2	
	55	39	19.0	14.2	
	37	this work	17.6	16.6	
	45	this work	16.8	15.5	
	55	this work	13.1	14.2	
n-octane	50.2	32	18.9	20.1	
	60	32	16.8	18.4	
	70.2	32	16.1	16.9	
	30	33	25.1	24.6	
	60	33	14.3	18.4	
	80	33	12.1	15.6	
	25	34	17.6	25.9	
	40	34	15.6	22.2	23.3
	50	34	14.1	20.1	
	60	34	13.4	18.4	
	30	35	21.6	24.6	
	20	37	33.4	27.4	
	25	37	33.6	25.9	
	30	37	31.1	24.6	
	35	37	30.9	23.3	
n-nonane	30	33	31.1	33.9	
	60	33	16.5	24.6	
	80	33	13.9	20.5	
	20	37	41.3	38.3	21.6
	25	37	41.0	36.0	
	30	37	38.6	33.9	
	35	37	37.2	32.0	
n-decane	60	33	20.1	32.8	66.2
	80	33	15.9	26.9	
2-methylbutane	24	31	13.6	9.40	22.0
	40	31	9.66	8.40	
2,2,4-trimethylpentane	50.2	32	17.8	21.4	
	60	32	16.0	19.6	26.5
	70.2	32	14.4	18.0	
	25	36	20.1	27.8	
cyclopentane	50.2	32	6.41	5.15	
	60	32	6.07	4.91	19.6
	70.2	32	5.84	4.68	
methylcyclopentane	50.2	32	8.41	7.19	
	60	32	7.92	6.78	
	70.2	32	7.50	6.41	
	25	34	9.10	8.49	8.6
	40	34	8.00	7.66	
	50	34	7.40	7.20	
	60	34	7.00	6.78	
cyclohexane	25	30	8.80	8.51	
	50.2	32	8.18	7.20	
	60	32	7.66	6.80	
	70.2	32	7.34	6.42	
	30	33	9.53	8.22	
	60	33	6.55	6.80	
	80	33	5.92	6.10	
	25	34	8.50	8.51	
	40	34	7.40	7.68	13.4
	50	34	6.80	7.21	
	60	34	6.40	6.80	
	30	35	8.52	8.22	
	25	36	9.09	8.51	
	20	37	13.3	8.83	
	25	37	13.4	8.51	
	30	37	12.6	8.22	
	35	37	12.6	7.94	
methylcyclohexane	50.2	32	9.67	9.92	
	60	32	9.14	9.27	
	70.2	32	8.64	8.67	
	30	33	11.5	11.6	
	60	33	7.70	9.27	
	80	33	6.98	8.17	14.0
	25	34	9.70	12.0	
	40	34	8.40	10.7	
	50	34	8.00	9.93	
	60	34	7.50	9.27	
	30	35	10.3	11.6	
ethylcyclohexane	30	33	14.4	16.2	
	60	33	9.41	12.6	26.3
	80	33	8.18	10.9	
	30	35	12.9	16.2	
n-propylcyclohexane	30	33	18.4	22.5	
	60	33	14.1	16.9	30.1
	80	33	9.73	14.4	
n-butylcyclohexane	30	33	24.2	31.1	45.0
	80	33	11.7	18.9	

ene–ethylene glycol at 20 °C. In Tables VII and VIII, which refer to nonaromatic and aromatic hydrocarbons, respectively, a comparison is made between experimental and predicted results in terms of the deviation D, defined by eq 4. Mean deviations of 66.3% and 12.7% were obtained for nonaromatic and aromatic hydrocarbons, respectively. The differences between experimental and predicted values are of the same order of magnitude as those obtained by Bastos et al. (*19*, *20*) for paraffins and aromatics in different solvents used in extractive distillation. The authors refer to mean deviations of 44.4% and

Table V. Comparison between Experimental Results and Predicted Values for Aromatic Hydrocarbons in NMP Using the UNIFAC Model

solute	temp, °C	ref	$\gamma^\infty_{\text{exptl}}$	$\gamma^\infty_{\text{calcd}}$	mean dev
benzene	25	23	1.03	1.20	
	25	30	1.02	1.20	
	50.2	32	1.27	1.26	
	60	32	1.23	1.28	
	70.2	32	1.28	1.29	
	30	33	1.09	1.21	
	60	33	1.44	1.28	
	80	33	1.17	1.31	
	25	34	1.00	1.20	
	40	34	1.00	1.24	
	50	34	1.00	1.26	
	60	34	1.00	1.28	
	30	35	1.08	1.21	
	25	36	0.997	1.20	
	20	37	1.49	1.18	
	25	37	1.60	1.20	14.3
	30	37	1.61	1.21	
	35	37	1.70	1.22	
	25	38	1.05	1.20	
	40	38	1.08	1.24	
	55	38	1.07	1.27	
	25	39	1.20	1.20	
	40	39	1.20	1.24	
	55	39	1.20	1.27	
	60	39	1.36	1.28	
	80	39	1.83	1.31	
	25	40	1.31	1.20	
	50	40	1.58	1.26	
	37	this work	1.22	1.23	
	45	this work	1.20	1.25	
	55	this work	1.10	1.27	
toluene	50.2	32	1.66	1.65	
	60	32	1.67	1.63	
	70.2	32	1.66	1.62	
	60	33	1.82	1.63	
	80	33	1.50	1.60	
	25	34	1.30	1.69	
	40	34	1.30	1.66	
	50	34	1.29	1.65	
	60	34	1.29	1.63	
	20	37	1.99	1.70	13.5
	25	37	2.17	1.69	
	30	37	2.16	1.68	
	35	37	2.27	1.67	
	25	39	1.70	1.69	
	40	39	1.70	1.66	
	55	39	1.60	1.64	
	37	this work	1.63	1.67	
	45	this work	1.4.	1.65	
	55	this work	1.40	1.64	
ethylbenzene	80	33	1.81	2.15	18.8

Table VI. Comparison between Experimental Liquid-Liquid Equilibrium Compositions and Predicted Ones Using the UNIFAC Model

system	ref	temp, °C	no. of data points	residuals,[a] % F_1	residuals,[a] % F_2
NMP/benzene/ n-heptane	38	25	5	0.71	7.5
NMP/toluene/ n-heptane	42	15	9	2.3	4.7
	42	25	10	0.62	6.2
	42	40	4	3.9	10
				md[b] 1.9	md[b] 7.1

[a] F_1 = UNIFAC parameters estimated by Ferreira et al. (*44*). F_2 = UNIFAC parameters estimated in this work. [b] Mean deviation.

23.9% for paraffins and aromatics, respectively. Figures 5 and 6 compare, for one of the mixtures considered, the new experimental results and those published in the open literature (*27*, *39*) with predictions by the UNIFAC model.

Table VII. Comparison between Experimental Results and Predicted Values for Nonaromatic Hydrocarbons in NMP/EG Mixtures Using the UNIFAC Model

mole fracn of EG	solute	temp, °C	$\gamma^\infty_{\text{exptl}}$	$\gamma^\infty_{\text{calcd}}$	dev *D*, %
0.220	*n*-hexane	37	21.4	11.9	44.3
		45	21.7	11.3	47.9
		55	22.3	10.6	52.3
	n-heptane	37	27.9	16.4	41.1
		45	28.0	15.5	44.7
		55	28.4	14.4	49.2
0.406	*n*-hexane	37	39.0	12.6	67.8
		45	36.9	12.0	67.4
		55	34.4	11.5	66.7
	n-heptane	37	51.1	17.4	65.9
		45	47.1	16.6	64.7
		55	43.2	15.7	63.7
0.495	*n*-hexane	37	53.2	13.3	74.9
		45	47.6	12.9	73.0
		55	41.7	12.3	70.4
	n-heptane	37	68.9	18.7	72.9
		45	61.1	17.9	70.7
		55	53.2	17.1	67.9
0.615	*n*-hexane	37	77.2	15.5	80.0
		45	65.4	15.0	77.0
		55	53.7	14.6	72.9
	n-heptane	37	107	22.1	79.4
		45	88.9	21.4	75.9
		55	71.6	20.6	71.2
0.827	*n*-hexane	37	127	30.4	76.1
		45	111	30.1	72.9
		55	94.4	29.7	68.5
	n-heptane	37	191	47.8	75.0
		45	160	47.2	70.5
		55	131	46.6	64.4
				md[a]	66.3

[a] Mean deviation.

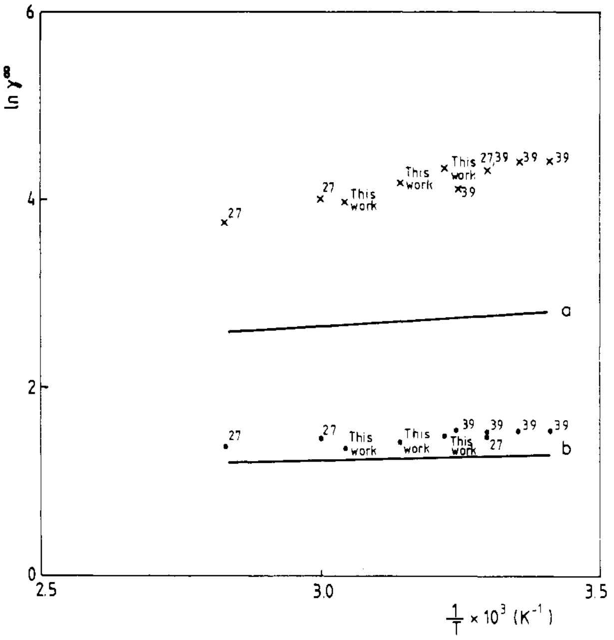

Figure 5. Activity coefficients at infinite dilution of *n*-hexane and benzene in NMP/EG mixture; mole fraction of EG = 0.615 (50 wt.%): ×, *n*-hexane; ●, benzene; a, predicted for *n*-hexane by UNIFAC model using VLE parameters (*45*) and parameters estimated in this work; b, predicted for benzene by UNIFAC model using VLE parameters (*45*) and parameters estimated in this work.

Conclusions

Experimental activity coefficients at infinite dilution were determined at 37, 45, and 55 °C for *n*-hexane, *n*-heptane, benzene, and toluene in NMP and in different mixtures of *N*-

Table VIII. Comparison between Experimental Results and Predicted Values for Aromatic Hydrocarbons in NMP/EG Mixtures Using the UNIFAC Model

mole fracn of EG	solute	temp, °C	$\gamma^{\infty}_{\text{exptl}}$	$\gamma^{\infty}_{\text{calcd}}$	dev D, %
0.220	benzene	37	1.52	1.62	6.8
		45	1.66	1.64	1.3
		55	1.85	1.65	10.6
	toluene	37	2.13	2.27	6.5
		45	2.34	2.41	4.2
		55	2.64	2.21	16.4
0.406	benzene	37	2.51	2.20	12.3
		45	2.55	2.21	13.5
		55	2.63	2.21	16.0
	toluene	37	3.57	3.19	10.5
		45	3.62	3.14	13.3
		55	3.71	3.08	17.0
0.495	benzene	37	3.14	2.63	16.3
		45	3.10	2.62	15.3
		55	3.07	2.62	14.7
	toluene	37	4.53	3.91	13.6
		45	4.44	3.84	13.5
		55	4.37	3.75	14.2
0.615	benzene	37	4.54	3.50	22.8
		45	4.20	3.48	17.2
		55	3.86	3.44	10.9
	toluene	37	6.82	5.47	19.8
		45	6.25	5.34	14.5
		55	5.67	5.19	8.4
0.827	benzene	37	7.27	7.31	0.5
		45	6.83	7.12	4.3
		55	6.40	6.90	7.8
	toluene	37	11.7	13.5	15.4
		45	10.9	13.0	19.4
		55	9.99	12.4	24.6
				md[a]	12.7

[a] Mean deviation.

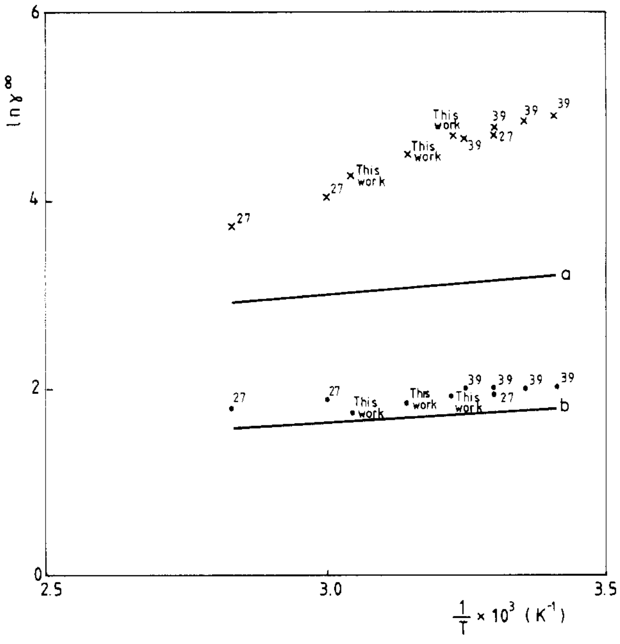

Figure 6. Activity coefficients at infinite dilution of *n*-heptane and toluene in NMP/EG mixture; mole fraction of EG = 0.615 (50 wt.%): ×, *n*-heptane; ●, toluene; a, predicted for *n*-heptane by UNIFAC model using VLE parameters (*45*) and parameters estimated in this work; b, predicted for toluene by UNIFAC model using VLE parameters (*45*) and parameters estimated in this work.

methylpyrrolidone and ethylene glycol.

A comparative analysis between the results obtained in this study and those published by other authors show that

(i) for *N*-methylpyrrolidone the numerical values of infinite dilution activity coefficients determined by different authors are in agreement (Figures 1 and 2); the values of Wardencki and Tameesh (*39*) and Müller et al. (*40*) (*n*-hexane, *n*-heptane) are however considerably higher;

(ii) for mixtures of *N*-methylpyrrolidone and ethylene glycol the values obtained in this study agree with the results reported in ref *27* and *39*.

A new set of UNIFAC parameters between the group NMP and the main groups CH_2, ACH, and $ACCH_2$ based on experimental infinite dilution activity coefficients was estimated.

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Glossary

B_{22}	second virial coefficient of solute
D	deviation defined by eq 4
F	measured flow of carrier gas, cm^3 s^{-1}, residual function defined by eq 5
M	number of experimental points
M_1	molecular weight of solvent, g mol^{-1}
P_{H_2O}	vapor pressure of water at the temperature T_f, mmHg
P_2^0	vapor pressure of the solute, mmHg
P_i	pressure at the inlet of the gas chromatographic column, mmHg
P_o	pressure at the outlet of the gas chromatographic column, mmHg
R	constant of ideal gases
T_{exptl}	experimental temperature, K
T_f	temperature of the film soap flow meter, K
t_a	retention time of air, s
t_r	retention time of solute, s
V_g^0	specific retention volume, cm^3 g^{-1}
v_2^0	molar volume of the solute, cm^3 mol^{-1}
x	liquid mole fraction
W_s	weight of solvent, g

Greek Letters

γ^{∞}	activity coefficient at infinite dilution

Superscripts

$\hat{}$	estimated values

Subscripts

calcd	calculated values
exptl	experimental values
i	component i
j	phase j
k	tie line k

Registry No. NMP, 872-50-4; EG, 107-21-1; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; benzene, 71-43-2; toluene, 108-88-3.

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Dynamic Viscosities of *n*-Alkanes and 2-Butanone Mixtures at 20 °C

Bernardo Celda, Rafael Gavara, Roberto Tejero, and J. E. Figueruelo*

Departamento Química Física, Facultad de Químicas, Universidad de Valencia, Burjasot (Valencia), Spain

Dynamic viscosities, η, of *n*-alkane + 2-butanone mixtures (*n*-alkane = *n*-heptane, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, and *n*-hexadecane) have been measured at 20 °C. Deviations from ideality, as defined by $\eta - \eta_{id}$ ($\eta_{id} \propto$ ideal viscosity), are negative in *n*-heptane + 2-butanone, null in *n*-nonane + 2-butanone, and positive in the remaining mixtures, increasing with the number of the carbon atoms of *n*-alkane. Qualitatively, these deivations seem to be related to entropic effects. $\eta - \eta_{id}$ values as calculated from excess volume, V^E, and excess free energy, G^E, data, according to the scheme of Bloomfield and Dewan, agree with experimental ones if absolute rate contributions are neglected.

Introduction

The interactions between the components of a mixed solvent mostly determine both the solubility in it of a polymer and the dimensions of the macromolecular coils in solution (*1*, *2*). *n*-Alkane + 2-butanone mixtures display interesting properties with respect to the solubility of polymers as evidenced by studies on total and preferential sorption equilibria of poly(dimethylsiloxane), PDMS, in those mixtures (*3*-*7*). On the one hand, the homologous series of the *n*-alkanes constitutes the best example of nonpolar liquids to which thermodynamic theories can be properly applied (*8*) and the solvent power for PDMS gradually decreases along the series, going from a very good solvent as *n*-heptane (HEP) to a nonsolvent as the *n*-hexadecane (HED) (*3*-*7*). On the other hand, 2-butanone (MEK) is the first member of the aliphatic ketone series which dissolves PDMS, at 20 °C being a θ solvent (*9*). *n*-Alkane + MEK mixtures provoke MEK autoassociation rupture and readily the mixtures show cosolvent character, i.e., larger solvent power than the pure liquids; the cosolvency increasing with the length of the hydrocarbon chain (*3*-*7*).

In the present paper, measurements of dynamic viscosity, η, at 20 °C for *n*-alkane + MEK mixtures with *n*-alkane = HEP, *n*-nonane (NON), *n*-decane (DEC), *n*-undecane (UND), *n*-dodecane (DOD), and HED are reported. The dynamic viscosity is an integral property of the liquid mixture which has been related to the interactions between liquids (*10*-*12*) and to the structure of the mixture (*11*, *13*, *14*). Our results are first qualitatively analyzed in light of both kinds of effects. Furthermore, a quantitative discussion is undertaken on grounds of the two major semiempirical theories of liquid viscosity, namely, the absolute rate and free volume theories following the theoretical scheme developed by Bloomfield and Dewan (*11*).

Experimental Section

All the organic liquids used in this study were of Merck origin and had nominal purities of 99.5% (MEK) and 99.0% (*n*-alkanes). The binary liquid mixtures were prepared by weighing the individual components with an accuracy of ±0.0001 g. The viscosities of the pure liquids and their mixtures were measured with two modified Ubbelohde viscometers, calibrated with benzene, doubly distilled water, and aqueous solutions of sucrose. Flow times were repeatedly determined, the standard

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