International Journal of Thermophysics, Vol. 2, No. 3, 1981

Transport Properties of Nonelectrolyte Liquid Mixtures—V. Viscosity Coefficients for Binary Mixtures of Benzene plus Alkanes at Saturation Pressure from 283 to 393 K

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Received March 16, 1981

Viscosity coefficient measurements at saturation pressure are reported for benzene + n-hexane, benzene + n-octane, benzene + n-decane, benzene + n-dodecane, benzene + n-hexadecane, and benzene + cyclohexane at temperatures from 283 to 393 K. The characteristic parameter G in the Grunberg and Nissan equation

$$\ell n\eta = x_1 \ell n\eta_1 + x_2 \ell n\eta_2 + x_1 x_2 G$$

is found to be both composition and temperature dependent for benzene + n-alkane mixtures, but it is independent of composition for the system benzene + cyclohexane.

KEY WORDS: viscosity; benzene; n-alkanes; cyclohexane; Grunberg and Nissan equation.

1. INTRODUCTION

The development of a successful molecular theory of transport properties in liquids and liquid mixtures is proving extremely difficult. As a consequence, the most satisfactory method of prediction of viscosity coefficients for binary liquid mixtures is based upon purely empirical equations, of which the Grunberg and Nissan equation [1] has been shown [2] to be the most effective.

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Table I. Viscosity Coefficients of Benzene

T (K)	ρ (kg · m^{-3})	η/ρ (mm^2 · s^{-1})	η (mN · s · m^{-2})	
			This work	Literature
283.15	889.8[a]	0.8564	0.7620	0.7574 [5], 0.7604 [8]
288.15	884.0[a]	0.7916	0.6998	0.6983 [5], 0.699 [9]
298.19	873.5	0.6893	0.6021	0.6007 [5], 0.603 [10]
313.23	857.5	0.5739	0.4921	0.4903 [5], 0.4922 [8]
333.36	835.4	0.4661	0.3894	0.388 [5]
353.29	813.2	0.3903	0.3174	0.317 [5], 0.317 [11]
373.28	790.7[a]	0.3344	0.2644	0.262 [11]
393.2	768.2[a]	0.2946	0.2263	0.218 [11]

[a] Extrapolated values.

In order to provide a critical test of this equation and of other methods for expressing mixture viscosity coefficient data, it is necessary to have accurate data over as wide a range of experimental conditions as possible. In a previous paper [3], sealed suspended-level viscometers were used to measure viscosity coefficients for n-hexane + n-hexadecane and for ternary and quaternary n-alkane mixtures at saturation pressure from 283 to 378 K. This paper reports measurements on benzene, cyclohexane, and n-decane, and binary mixtures of benzene + n-hexane, benzene + n-octane, benzene + n-decane, benzene + n-dodecane, benzene + n-hexadecane, and benzene + cyclohexane at saturation pressure from 283 to 393 K. The results are used to determine the composition and temperature dependence of the characteristic parameter G in the Grunberg and Nissan equation.

Table II. Viscosity Coefficients of Cyclohexane

T (K)	ρ (kg · m^{-3})	η/ρ (mm^2 · s^{-1})	η (mN · s · m^{-2})	
			This work	Literature
283.15	787.9[a]	1.4991	1.181	1.176 [5]
288.15	783.2[a]	1.3719	1.074	1.070 [5], 1.065 [9]
298.19	773.8	1.1587	0.8966	0.894 [5], 0.8856 [12]
313.23	759.5	0.9252	0.7027	0.701 [5], 0.701 [9]
333.36	739.9	0.7143	0.5285	0.525 [5]
353.29	719.7	0.5737	0.4129	0.409 [5]
373.28	699.3[a]	0.4728	0.3306	
393.2	678.3[a]	0.4008	0.2719	

[a] Extrapolated values.

Table III. Viscosity Coefficients of n-Decane

T (K)	ρ ($kg \cdot m^{-3}$)	η/ρ ($mm^2 \cdot s^{-1}$)	η ($mN \cdot s \cdot m^{-2}$) This work	η ($mN \cdot s \cdot m^{-2}$) Ref. [5]
283.15	737.4[a]	1.4595	1.076	1.087
288.15	733.7[a]	1.3502	0.9906	1.001
298.19	726.3	1.1718	0.8511	0.8583
313.23	714.9	0.9669	0.6912	0.6981
333.36	699.6	0.7750	0.5422	0.5489
353.29	684.2[a]	0.6418	0.4391	0.4457
373.28	668.1[a]	0.5428	0.3626	0.3700
393.2	651.6[a]	0.4686	0.3053	0.3127

[a] Extrapolated values.

2. EXPERIMENTAL

The suspended-level viscometers have been fully described elsewhere [3]. They were sealed with a Rotaflo tap to allow measurements to be made at temperatures above the normal boiling point. All liquids were filtered through a millipore syringe filter before entering the viscometer. The apparatus was then placed in a low temperature bath, and the space above the liquid was evacuated so that the liquid was under its own vapor pressure. Flow-time measurements were made for each liquid in two viscometers having different dimensions to obtain a more reliable estimate of the precision of the results. Temperature control was better than 0.02 K.

The viscometers had been calibrated [3] using benzene, cyclohexane, n-dodecane, and n-hexadecane at different temperatures, for which kinematic viscosity coefficients had been measured in a master viscometer. The follow-

Table IV. Viscosity Coefficients for Mixtures of Benzene (1) + n-Hexane (2)

T (K)	x(1)	ρ ($kg \cdot m^{-3}$)	η ($mN \cdot s \cdot m^{-2}$)
283.15	0.4995	755.4	0.4193
288.15	0.4995	750.6	0.3963
298.19	0.4997	741.0	0.3561
313.23	0.4999	726.5	0.3062
333.36	0.5002	706.4	0.2545
353.29	0.5007	685.5	0.2163
373.28	0.5013	664.2	0.1857

Table V. Viscosity Coefficients for Mixtures of Benzene (1) + n-Octane (2)

T (K)	$x(1)$	ρ (kg · m^{-3})	η (mN · s · m^{-2})	$x(1)$	ρ (kg · m^{-3})	η (mN · s · m^{-2})
283.15	0.2539	736.0	0.5838	0.5041	769.6	0.5773
288.15	0.2539	731.8	0.5491	0.5041	765.1	0.5414
298.19	0.2536	723.4	0.4863	0.5037	756.2	0.4803
313.23	0.2533	710.5	0.4132	0.5034	742.6	0.4068
333.36	0.2527	693.1	0.3383	0.5027	724.1	0.3335
353.29	0.2518	675.3	0.2825	0.5016	705.6	0.2786
373.28	0.2503	657.1	0.2394	0.4999	686.6	0.2363
393.2	0.2482	638.2	0.2051	0.4975	667.2	0.2044
283.15	0.6746	800.2	0.5938	0.8255	835.5	0.6357
288.15	0.6746	795.5	0.5567	0.8255	830.6	0.5941
298.19	0.6743	786.1	0.4917	0.8253	820.7	0.5207
313.23	0.6741	771.9	0.4151	0.8252	805.8	0.4359
333.36	0.6735	752.6	0.3393	0.8249	785.6	0.3524
353.29	0.6726	732.7	0.2823	0.8243	764.8	0.2923
373.28	0.6713	712.4	0.2390	0.8236	743.5	0.2458
393.2	0.6694	691.3	0.2062	0.8224	721.6	0.2105

ing general equation was used:

$$\eta/\rho = A(1 - \rho_v/\rho)\,(1 + \alpha\Delta T)\,t - B/t \tag{1}$$

where A and B are apparatus constants, t is the flow time, ρ and ρ_v are the densities of liquid and vapor, α is the coefficient of linear thermal expansion of glass, ΔT is taken as $(T - 313.2)$, and η is the dynamic viscosity coefficient.

Table VI. Viscosity Coefficients for Mixtures of Benzene (1) + n-Decane (2)

T (K)	$x(1)$	ρ (kg · m^{-3})	η (mN · s · m^{-2})
283.15	0.4991	780.5	0.8086
288.15	0.4991	776.3	0.7525
298.19	0.4986	767.9	0.6561
313.23	0.4982	755.2	0.5456
333.36	0.4972	737.6	0.4387
353.29	0.4956	720.0	0.3617
373.28	0.4931	701.8	0.3031
393.2	0.4895	682.9	0.2585

It was concluded from a comparison of measured viscosity coefficients for n-hexane with recent literature values [4] that the results obtained using these sealed suspended-level viscometers should be accurate to ±0.5%, except at temperatures where the kinematic viscosity coefficient was less than 0.4 $\mathrm{mm^2 \cdot s^{-1}}$, where the accuracy is estimated to be ±1%.

3. MATERIALS

n-Hexane, n-octane, n-decane, n-dodecane, n-hexadecane, and cyclohexane were purchased from British Drug Houses Ltd., Poole, England. All had a stated purity of 99+ mol%, except n-decane, which was 98+ mol%. UltraR benzene was supplied by Hopkin and Williams Ltd. Freezing-point determinations indicated that the purity of the n-hexadecane was 99.6 mol%. Fractional freezing of this compound and fractional distillation of the other hydrocarbons produced fractions whose measured refractive indices and densities are in close agreement with literature values, as shown in Table II of ref. [3]. For n-decane, $n(D, 298.15\ \mathrm{K})$ was found to be 1.40956, which agrees closely with the value of 1.40967 [5]. Its measured density was 726.3 $\mathrm{kg \cdot m^{-3}}$, in excellent agreement with the reported value [6] of 726.25 $\mathrm{kg \cdot m^{-3}}$.

Table VII. Viscosity Coefficients for Mixtures of Benzene (1) + n-Dodecane (2)

T (K)	$x(1)$	ρ $(\mathrm{kg \cdot m^{-3}})$	η $(\mathrm{mN \cdot s \cdot m^{-2}})$	$x(1)$	ρ $(\mathrm{kg \cdot m^{-3}})$	η $(\mathrm{mN \cdot s \cdot m^{-2}})$
283.15	0.2509	769.4	1.443	0.4994	789.1	1.129
288.15	0.2509	765.7	1.317	0.4994	785.0	1.040
298.19	0.2504	758.1	1.108	0.4988	776.9	0.8917
313.23	0.2500	746.6	0.8848	0.4983	764.5	0.7258
333.36	0.2490	731.0	0.6814	0.4973	748.0	0.5703
353.29	0.2473	715.6	0.5445	0.4954	731.2	0.4626
373.28	0.2446	699.7	0.4460	0.4925	714.3	0.3834
393.2	0.2408	683.6	0.3739	0.4882	697.1	0.3243
283.15	0.7498	822.0	0.8795			
288.15	0.7498	817.5	0.8143			
298.19	0.7495	808.5	0.7079			
313.23	0.7492	795.0	0.5854			
333.36	0.7485	776.6	0.4668			
353.29	0.7474	758.0	0.3831			
373.28	0.7457	739.1	0.3200			
393.2	0.7431	719.8	0.2725			

4. RESULTS

Values for the kinematic viscosity coefficient, density, and dynamic viscosity coefficient are given in Table I for benzene, in Table II for cyclohexane, and in Table III for n-decane. For the mixtures, compositions, densities, and dynamic viscosity coefficients are reported in Table IV for benzene + n-hexane, in Table V for benzene + n-octane, in Table VI for benzene + n-decane, in Table VII for benzene + n-dodecane, in Table VIII for benzene + n-hexadecane, and in Table IX for benzene + cyclohexane. Densities were measured at 298 K using a calibrated Lipkin pyknometer and at higher temperatures using a sealed volume change apparatus [7]. They are considered to be accurate to ±0.3 $\text{kg} \cdot \text{m}^{-3}$ up to 333 K and to ±0.5 $\text{kg} \cdot \text{m}^{-3}$ at higher temperatures.

From a comparison of the present viscosity results with literature values for benzene [5, 8–11], cyclohexane [5, 9, 12], and n-decane [5], it is found that there is excellent agreement for benzene and cyclohexane. For n-decane, the literature values are too high by up to 2.5%. A similar discrepancy has previously been noted [3] with API 44 values [5] for other n-alkanes. For the mixtures, corrections were made to the liquid compositions to take into account the liquid-vapor equilibrium at each temperature.

5. GIBBS FREE ENERGY OF ACTIVATION FOR FLOW

On the basis of the Eyring activation theory of transport properties [13], a molar excess Gibbs free energy of activation for flow $\Delta^* G^E$ can be derived

Table VIII. Viscosity Coefficients for Mixtures and Benzene (1) + n-Hexadecane (2)

T (K)	$x(1)$	ρ ($\text{kg} \cdot \text{m}^{-3}$)	η ($\text{mN} \cdot \text{s} \cdot \text{m}^{-2}$)	$x(1)$	ρ ($\text{kg} \cdot \text{m}^{-3}$)	η ($\text{mN} \cdot \text{s} \cdot \text{m}^{-2}$)
298.19	0.1211	773.5	2.682	0.2858	779.4	2.189
313.23	0.1207	762.9	1.968	0.2852	768.5	1.652
333.36	0.1199	748.7	1.398	0.2839	753.8	1.197
353.29	0.1186	734.6	1.051	0.2817	739.0	0.9154
373.28	0.1165	720.4	0.8212	0.2782	724.3	0.7274
393.2	0.1134	706.2	0.6650	0.2730	709.6	0.5932
298.19	0.5976	797.8	1.369	0.8497	829.6	0.8411
313.23	0.5971	785.9	1.078	0.8495	815.9	0.6797
333.36	0.5960	769.8	0.8185	0.8491	797.4	0.5351
353.29	0.5940	753.4	0.6514	0.8483	778.4	0.4353
373.28	0.5910	736.5	0.5300	0.8472	759.2	0.3630
393.2	0.5864	719.4	0.4580	0.8454	739.5	0.3071

Table IX. Viscosity Coefficients for Mixtures of Benzene (1) + Cyclohexane (2)

T (K)	x(1)	ρ (kg · m^{-3})	η (mN · s · m^{-2})	x(1)	ρ (kg · m^{-3})	η (mN · s · m^{-2})
283.15	0.1991	801.6	0.9348	0.4020	819.1	0.8055
288.15	0.1991	796.9	0.8653	0.4020	814.2	0.7468
298.19	0.1989	787.3	0.7346	0.4017	804.4	0.6427
313.23	0.1987	772.7	0.5916	0.4014	789.5	0.5268
333.36	0.1982	752.8	0.4586	0.4007	769.2	0.4161
353.29	0.1975	732.1	0.3668	0.3995	748.0	0.3377
373.28	0.1969	711.1	0.2989	0.3977	726.7	0.2788
393.2	0.1944	689.9	0.2503	0.3950	704.5	0.2348
283.15	0.6004	839.0	0.7431	0.7949	861.3	0.7269
288.15	0.6004	834.0	0.6903	0.7949	856.2	0.6734
298.19	0.6001	823.8	0.5977	0.7947	845.8	0.5825
313.23	0.5998	808.6	0.4928	0.7945	830.2	0.4809
333.36	0.5991	788.0	0.3923	0.7941	809.1	0.3832
353.29	0.5980	766.4	0.3203	0.7934	787.0	0.3129
373.28	0.5963	744.8	0.2662	0.7922	764.7	0.2608
393.2	0.5936	722.7	0.2270	0.7905	741.6	0.2227
283.15	0.8779	872.2	0.7319			
288.15	0.8779	867.0	0.6778			
298.19	0.8778	856.4	0.5859			
313.23	0.8777	840.6	0.4826			
333.36	0.8774	819.2	0.3840			
353.29	0.8769	797.5	0.3147			
373.28	0.8762	775.4	0.2633			

from experimental viscosity coefficient data, according to

$$\Delta^*G^E = RT\{\ell\text{n}(\eta V) - \Sigma x_i \ell\text{n}(\eta_i V_i)\} \qquad (2)$$

Values of Δ^*G^E for these benzene + n-alkane systems are shown in Fig. 1. At 298.19 K, Δ^*G^E is negative for benzene + n-hexane, benzene + n-octane, and benzene + n-decane and becomes increasingly positive on passing from benzene + n-dodecane to benzene + n-hexadecane at a given mole fraction of benzene. An increase in temperature causes Δ^*G^E to become less negative, or more positive.

For n-alkane binary mixtures, the principle of congruence has been applied [14] to Δ^*G^E, and this forms the basis of an accurate method for predicting mixture viscosity coefficients using Eq. (2), not only at 298 K but also at other temperatures [3]. The principle of congruence does not apply to benzene + n-alkane systems, and it is necessary to have plots of Δ^*G^E versus

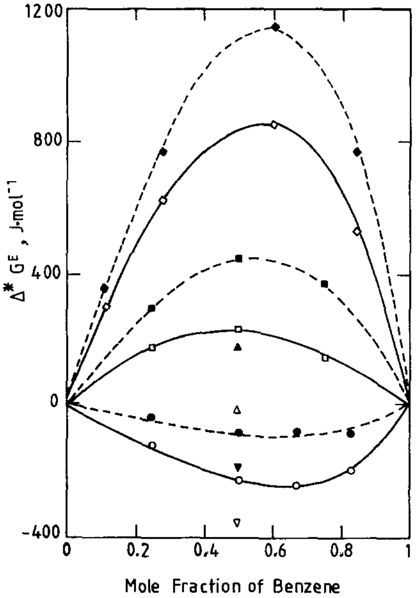

Fig. 1. Effect of temperature on $\Delta^* G^E$ for benzene plus n-alkane mixtures. ———, 298 K; - - -, 373 K; ▽, plus n-hexane; ○, plus n-octane; △, plus n-decane; □, plus n-dodecane; ◇, plus n-hexadecane.

carbon number of the n-alkane for the given temperature and composition in order to make a reliable estimate of $\Delta^* G^E$ for other benzene + n-alkane mixtures. Such plots are shown in Fig. 2 for equimolar mixtures at 298 K and 373 K. Viscosity coefficients can then be calculated from Eq. (2) with an estimated accuracy for 1 or 2%.

6. THE GRUNBERG AND NISSAN EQUATION

This purely empirical equation may be written

$$\ell n \eta = x_1 \ell n \eta_1 + x_2 \ell n \eta_2 + x_1 x_2 G \quad (3)$$

where G is the characteristic parameter. For binary benzene + n-alkane mixtures, G is composition and temperature dependent as shown in Fig. 3. The system which is closest to ideal ($G = 0$) at these temperatures is benzene + n-dodecane. For mixtures where the n-alkane has a carbon number less than 12, G is negative. An increase in temperature results in G becoming less negative, and the composition dependence decreases. Where the n-alkane chain has more than 12 carbon atoms, G is positive for the benzene + n-alkane mixtures. It becomes larger as the temperature is increased and has a greater composition dependence. By contrast, for the benzene + cyclohex-

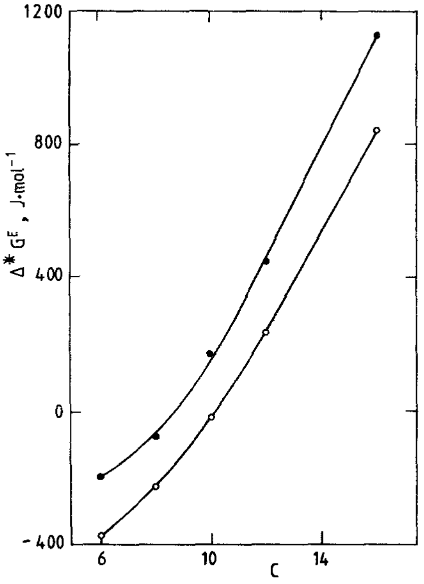

Fig. 2. Variation in $\Delta^* G^E$ with n-alkane chain length for equimolar benzene plus n-alkane mixtures: ○, 298 K; ●, 373 K.

ane system, the composition dependence of G is practically zero at each temperature, but there is a significant temperature dependence, with G becoming less negative as the temperature is raised.

For the accurate representation of viscosity coefficients of benzene + n-alkane and benzene + cyclohexane mixtures by Eq. (3), it is essential to take into account the composition and temperature dependence of G. Of the two effects, the temperature dependence is more important since, for example, if the 298 K values for G for the equimolar mixtures are used to calculate the corresponding mixture viscosity coefficients at 373 K, the resulting values will differ from the measured coefficients by up to 8%. However, if the equimolar value of G for any given system at a constant temperature is used to calculate viscosity coefficients at other compositions, the results differ from the experimental values by only 2% at most, for benzene + n-hexane at 298 K and for benzene + n-hexadecane at 373 K, where the composition dependence is greatest.

Figure 4 illustrates the variation in G with alkane chain length for equimolar benzene + n-alkane mixtures at 298.19 and 373.28 K. There is a smooth variation in G with increasing chain length, and above C_{10}, this becomes effectively linear. From such plots at different temperatures, a value for G can be read for any benzene + n-alkane system with alkane chain length between 6 and 16, and the viscosity coefficient for any composition at a given temperature calculated from Eq. (3) will have an estimated accuracy of 2%.

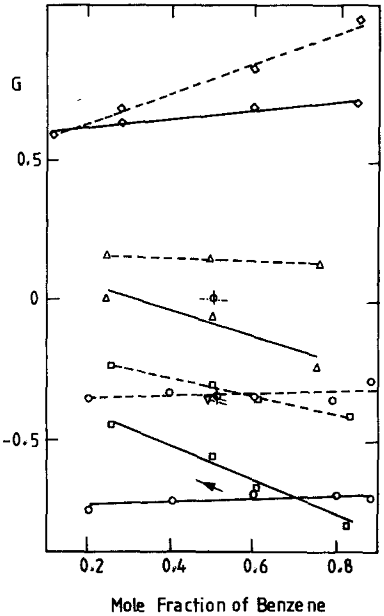

Fig. 3. Dependence of G on mole fraction and temperature for binary mixtures containing benzene. ——, 298 K; ---, 373 K; ○, plus cyclohexane; ∇, plus n-hexane; □, plus n-octane; =, plus n-decane; ϕ, plus n-dodecane; ◇, plus n-hexadecane.

Since Eq. (3) is empirical, any physical significance that may be attached to the parameter G is obscure, and attempts to relate its values to other defined physical properties have not been successful. However, systematic variations with chemical structure have been observed in limited groups [15], and this offers promise as a useful predictive method, especially for multicomponent mixtures.

7. CONCLUSIONS

Viscosity coefficient measurements at saturation pressure are reported for benzene, cyclohexane, n-decane, and binary mixtures of benzene + n-hexane, benzene + n-octane, benzene + n-decane, benzene + n-dodecane, benzene + n-hexadecane and benzene + cyclohexane from 283 to 393 K with an estimated accuracy of ±0.5%, except for liquids, where the kinematic viscosity is less than 0.4 $mm^2 \cdot s^{-1}$ when the accuracy is ±1%. For the binary mixtures, the Grunberg and Nissan equation satisfactorily represents the data at all temperatures, but the characteristic G is both composition and temperature dependent for the benzene + n-alkane systems and temperature dependent for the benzene + cyclohexane system. When the temperature dependence is taken into account, G values derived for the equimolar mixtures can be used to predict viscosity coefficients for benzene + n-alkane mixtures, where the n-alkane carbon number lies between 6 and 16, and for

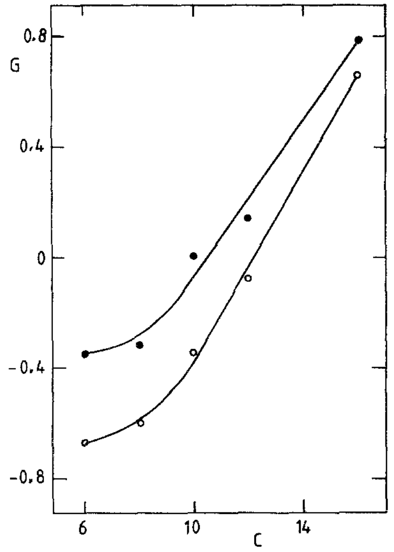

Fig. 4. Variation in the Grunberg and Nissan constant with n-alkane chain length for equimolar benzene plus n-alkane mixtures: ○, 298 K; ●, 373 K.

benzene + cyclohexane mixtures, of any composition with an estimated accuracy of ±2%.

ACKNOWLEDGMENT

Support from the Science Research Council through the CASE Awards Scheme is gratefully acknowledged.

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